VOL.
17
1962

TETRAHEDRON

THE INTERNATIONAL JOURNAL OF ORGANIC CHEMISTRY

FOUNDED BY SIR ROBERT ROBINSON

HONORARY REGIONAL EDITORS

Prof. R. H. MARTIN: Laboratoires de Chimie Organique, Université Libre de Bruxelles, 50 Ave. F. D. Roosevelt, Brussels, Belgium.
Prof. A. N. NESMEYANOV: Akademiya Nauk SSSR, Bolshaya Kaluzhskaya 14, Moscow, U.S.S.R.
Prof. H. H. WASSERMAN: 1901-A Yale Station, New Haven, Connecticut, U.S.A.
Prof. F. WEYGAND: Organisch-chemisches Institut, Technische Hochschule, München 2, Germany.

EXECUTIVE EDITOR

Prof. H. STEPHEN: 79 Hurst Rise Road, Cumnor Hill, Oxford, England.

HONORARY EDITORIAL ADVISORY BOARD

Europe

O. ACHMATOWICZ—Warsaw
K. BALENOVIĆ—Zagreb
D. H. R. BARTON—London
ENDRE BERNER—Oslo
A. J. BIRCH—Manchester
J. W. CORNFORTH—London
C. DUFRAISSE—Paris
H. ERDTMAN—Stockholm
G. FODOR—Budapest
C. A. GROB—Basel
E. HAVINGA—Leiden
B. HELFERICH—Bonn
M. JULIA—Paris
G. W. KENNER—Liverpool
E. LEDERER—Paris
R. P. LINSTEAD—London
M. LORA-TAMAYO—Madrid
G. OURISSON—Strasbourg
R. PAUL—Paris
V. PRELOG—Zurich
A. QUILICO—Milano
R. ROBINSON—London (Co-Chairman)
L. RUZICKA—Zurich
F. SORM—Prague
M. STACEY—Birmingham
A. TODD—Cambridge
W. TREIBS—Heidelberg
T. URBAŃSKI—Warsaw
S. VEIBEL—Copenhagen
L. VELLUZ—Paris
F. WESSELY—Vienna
T. S. WHEELER—Dublin
O. WICHTERLE—Prague
G. WITTIG—Heidelberg

American Continents

P. D. BARTLETT—Cambridge, Mass.
H. C. BROWN—Lafayette
V. DEULOFEU—Buenos Aires
M. J. S. DEWAR—Chicago
C. DJERASSI—Stanford
W. DOERING—New Haven
W. S. JOHNSON—Stanford
L. MARION—Ottawa
J. D. ROBERTS—Pasadena
A. SANDOVAL—Mexico
G. STORK—New York
A. WEISSBERGER—Rochester
K. WIESNER—New Brunswick
S. WINSTEIN—Los Angeles
R. B. WOODWARD—Cambridge, Mass. (Co-Chairman)

The East

E. D. BERGMANN—Tel-Aviv
L. H. BRIGGS—Auckland
D. GINSBURG—Haifa
HUANG-MINLON—Shanghai
T. R. SESHADRI—Delhi
C. W. SHOPPEE—Sydney
F. SONDHEIMER—Rehovoth
S. SUGASAWA—Tokyo
K. TAKEDA—Japan
K. VENKATARAMAN—Poona

Secretary to the Board of Editors: Dr. T. STEPHEN, 79 Hurst Rise Road, Cumnor Hill, Oxford.

VOLUME 17

Copyright © 1962 Pergamon Press Ltd.

PERGAMON PRESS LTD.

OXFORD LONDON NEW YORK PARIS

NOTES FOR CONTRIBUTORS

Submission of Original Contributions

Tetrahedron is intended to cover all aspects of organic chemistry, whether theoretical or practical, analytical or synthetic, physical or biological. *Tetrahedron* publishes articles in English, French and German, but will arrange to have papers submitted in any other language translated by Pergamon Institute into English. They should be submitted for publication to the appropriate Honorary Regional Editor or, in cases of contributions emanating from areas not so covered, to the Executive Editor:

Professor William Doering (for the Western Hemisphere), 1901-A Yale Station, New Haven, Connecticut, U.S.A.

Professor R. H. Martin (contributions in the French language), Laboratoires de Chimie Organique, Université Libre de Bruxelles, 50 Ave. F. D. Roosevelt, Brussels, Belgium.

Professor A. N. Nesmeyanov (for the U.S.S.R. and Eastern Europe), Akademiya Nauk SSSR, Bolshaya Kaluzhskaya 14, Moscow, U.S.S.R.

Professor H. Stephen, The Executive Editor, 79 Hurst Rise Road, Cumnor Hill, Oxford, England.

Professor Dr. F. Weygand (contributions in the German language), Organisch-chemisches Institut, Technische Hochschule, München 2, Germany.

Note: The contents of papers shall be the sole responsibility of the authors and publication shall not imply the concurrence of editors or publishers.

Form of Contributions

Manuscripts should be submitted in duplicate, double-spaced typescript. Contributions should be prepared in the form generally accepted for publication in the national journals. *Papers* should include an abstract in which the essential contents are briefly recapitulated. The abstract should be in the language of the paper, but for French or German papers an English version should also be provided. On the basis of originality, significance and breadth of interest to an international audience, *papers* are of the usual form reporting the result of original work. *Tetrahedron* offers an author the opportunity of including a longer review of his own published work, particularly if the paper represents the completion of a phase of a larger investigation.

Preliminary Communications are invited. An immediate decision on the acceptability of such contributions will be made by the receiving Editor, and publication in the next available issue is assured.

Preliminary Communications should now be submitted to Tetrahedron Letters.

Preparation of Manuscript

Typographical correctness in the printing proofs is better assured by following the suggestions below in regard to mathematical expressions and other formulae.

Letters to be set in Greek type should be clearly indicated.

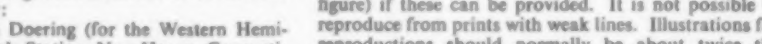
Confusion between the letter *l* and the numeral 1 when standing alone can be avoided by looping the letter *l* when typewritten. Similar differentiation between the O (or o) and zero 0 is advisable.

Subscripts and superscripts should be clearly indicated. Primes (as ρ') should be written or identified so that they will not be interpreted as the superior figure 1 (ρ^1).

In general, equations and formulae should be clearly and carefully written, taking care to have all figures and symbols, especially in fractions and equations, in the alignment in which they are to be printed. It would be helpful to have a third set of structural formulae attached.

Nomenclature following the I.U.P.A.C. Commission rules will always be accepted without modification. Otherwise the Editor's function in these matters will be advisory in nature.

Figures and illustrations should be separate from the typescript of the paper and should be clearly identified on the back by the author's name, the abbreviated title of the paper and the figure number. Legends should also be typed on a separate sheet. Line drawings which require re-drawing should include all relevant details and clear instructions for the draughtsman. If figures are already well drawn, it may be possible to reproduce them directly from the originals, or from good photoprints (preferably twice the size of the final published figure) if these can be provided. It is not possible to reproduce from prints with weak lines. Illustrations for reproductions should normally be about twice the final size required and the lettering and figures on them should be large enough to be clear when so reduced. Photographs should be included only where they are absolutely essential. The following standard symbols should be used on line drawings since they are easily available to the printers:



Tables should be so constructed as to be intelligible without reference to the text. Every table and column should be provided with an explanatory heading. Units of measure must always be clearly indicated. The same data should not be reproduced in both tables and figures.

References and footnotes should be numbered consecutively in the text and should be inserted immediately following their first introduction. Full references should be given as numbered footnotes, containing the names of all the authors, preceded by initials, title of journal (preferably abbreviated in accordance with current *Tetrahedron* practice), volume number, first page number and year, in the following way:

[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.* **55**, 661 (1933).

[2] J. R. Goldsmith, D. L. Graft and O. I. Joensuu, *Geochim. et Cosmochim. Acta* **7**, 221 (1955).

[3] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds* Vol. II, p. 239. Pergamon Press, London (1956).

Abbreviations are used freely in *Tetrahedron*, particularly in setting the experimental section. For the most part these are not followed by a full stop (period). Among the more commonly used abbreviations, these may be listed:

g kg mm cm ml cc cm^3 sec min hr n_D^{25} $[\alpha]_D^{25}$ 25° (without C which is always understood) but m.p., b.p., l. (litre), in. (inch) but in^3.

New compounds should be indicated by underlining the name (for italics) at its first mention (including headings) in the experimental section only, and by giving analytical results in the form: (Found: C, 62·9; H, 5·4. $C_{12}H_{12}O_4N$ requires: C, 63·2; H 5·3%).

Analytical results for compounds which have previously been adequately described in the literature should be given in the form: (Found: C, 62·9; H, 5·4. Calc. for $C_{12}H_{12}O_4N$: C, 63·2; H, 5·3%). The punctuation should be noted.

Proofs and Reprints

Proofs will be sent to authors for correction when their contribution is first set, but there is rarely time for page proofs also to be sent for checking. This will be done, however, where the amount of alteration makes it advisable. Proofs of text, and illustrations which cannot be set in type, will not be received simultaneously. Twenty-five free *reprints* (without covers) of papers having one author will be provided. Where there is more than one author, each additional author will receive 10 free reprints. Additional copies can be obtained if ordered when proofs are returned. A reprint order form will accompany first proofs.

VOL.
17
1962

LIST OF CONTENTS

CONTRIBUTED SYMPOSIA ON RECENT DEVELOPMENTS IN ORGANIC CHEMISTRY

VOLUME 17

NUMBERS 1/2

Symposium 2. New Reactions and New Classes of Compounds

List of Contributors iii

Foreword 1

R. HUISGEN, M. SEIDEL, G. WALLBILLICH und H. KNUPFER: Diphenylnitrilimin und seine 1.3-Dipolaren Additionen an Alkene und Alkine 3

R. W. WHITE and W. D. EMMONS: The chemistry of permaleic acid . . 31

A. L. NUSSBAUM and C. H. ROBINSON: Some recent developments in the preparative photolysis of organic nitrites 35

A. N. NESMEYANOV, R. KH. FRIEDLINA, E. C. CHUKOVSKAYA, R. G. PETROVA and A. B. BELYAVSKY: Addition, substitution, and telomerization reactions of olefins in the presence of metal carbonyls or colloidal iron 61

A. N. NESMEYANOV, R. KH. FRIEDLINA, V. N. KOST, T. T. VASSILYEVA and B. V. KOPYLOVA: Synthesis of α-chlorocarboxylic acids by chlorinating compounds containing the CCl_2—CH group in acid medium 69

C. O. PARKER, W. D. EMMONS, H. A. ROLEWICZ and K. S. MCCALLUM: Chemistry of dinitroacetonitrile—I. Preparation and properties of dinitroacetonitrile and its salts 79

C. O. PARKER, W. D. EMMONS, A. S. PAGANO, H. A. ROLEWICZ and K. S. MCCALLUM: Chemistry of dinitroacetonitrile—II. Derivatives of dinitroacetonitrile from Michael, Mannich and alkylation reactions. 2,2-Dinitro-2-cyanoethanol and its derivatives 89

C. O. PARKER: Chemistry of dinitroacetonitrile—III. Dinitroacetamide and its derivatives 105

C. O. PARKER: Chemistry of dinitroacetonitrile—IV. Preparation and properties of esters of dinitrocyanoacetic acid 109

M. F. HAWTHORNE: Amine boranes—X. Alkylideneamino t-butylboranes. The hydroboration of nitriles with trimethylamine t-butylborane . . 117

NUMBERS 3/4

Symposium 3. An Epistologue on the Effect of Environment on the Properties of Carbon Bonds

List of Contributors iii

M. J. S. DEWAR: Introduction. Epistologue on the effect of environment on the properties of carbon bonds 123

D. R. LIDE Jr: A survey of carbon-carbon bond lengths 125

B. P. STOICHEFF: The variation of carbon-carbon bond lengths with environment as determined by spectroscopic studies of simple polyatomic molecules . . 135

O. BASTIANSEN and M. TRAETTEBERG: The nature of bonds between carbon atoms. How they vary with environment 147

D. W. J. CRUICKSHANK: X-ray results on aromatic hydrocarbons 155

D. J. MARAIS, N. SHEPPARD and B. P. STOICHEFF: An investigation of the structure of butadiene by high resolution infra-red and raman spectroscopy 163

L. OLEARI: Electronic wave function of methane and C—H bond orbital - . 171

L. S. BARTELL: On inferences of bond character from bond length. The important role of nonbonded interactions 177

E. BRIGHT WILSON Jr: Conjugation, hybridization, and steric hindrance in relation to bond lengths 191

W. M. SCHUBERT, R. B. MURPHY and J. ROBINS: Election donor and acceptor properties of alkyl substituents 199

C. A. COULSON and W. T. DIXON: Bond lengths in cyclic polyenes $C_{2n}H_{2n}$. A re-examination from the valence-bond point of view 215

L. PAULING: The carbon–carbon triple bond and the nitrogen–nitrogen triple bond 229

I. FISCHER-HJALMARS: On the nature of bonds between carbon atoms . . 235

M. I. KABACHNIK, T. A. MASTRYUKOVA and T. A. MELENT'YEVA: Conjugation in systems with a tetrahedral atom diarylphosphinic acids 239

R. DAUDEL: Remarks concerning the effect of environment on the properties of CC and CO bonds 243

Discussion 247

VOL.
17
1962

VOL
17
196

TETRAHEDRON

Contributed Symposia on Recent Developments in Organic Chemistry

VOL.
17
1962

Number 2

NEW REACTIONS AND NEW CLASSES OF COMPOUNDS

Convened and Edited by

M. F. HAWTHORNE

The University of California, Riverside, California, U.S.A.

VOL.
17
1962

Contributors to the Tetrahedron Symposium on New Reactions and New Classes of Compounds

A. B. BELYAVSKY, Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

E. C. CHUKOVSKAYA, Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

W. D. EMMONS, Rohm & Haas Co., Research Laboratory, Philadelphia 37, Pennsylvania, U.S.A.

R. KH. FREIDLINA, Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

M. F. HAWTHORNE, University of California, Riverside, California, U.S.A.

R. HUISGEN, Institut für Organische Chemie der Universität Munchen, Germany.

B. V. KOPYLOVA, Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

V. N. KOST, Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, Moscow U.S.S.R.

H. KNUPFER, Institüt fur Organische Chemie der Universität Munchen, Germany.

K. S. MCCALLUM, Rohm & Haas Co., Redstone Arsenal Research Division, Huntsville, Alabama, U.S.A.

A. N. NESMEYANOV, Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

A. L. NUSSBAUM, Natural Products Research Department, Schering Corporation, Bloomfield, New Jersey, U.S.A.

A. S. PAGANO, Rohm & Haas Co., Redstone Arsenal Research Division, Huntsville, Alabama, U.S.A.

C. O. PARKER, Rohm & Haas Co., Redstone Arsenal Research Division, Huntsville, Alabama, U.S.A.

R. G. PETROVA, Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

C. H. ROBINSON, Natural Products Research Department, Schering Corporation, Bloomfield, New Jersey, U.S.A.

H. A. ROLEWICZ, Rohm & Haas Co., Redstone Arsenal Research Division, Huntsville, Alabama, U.S.A.

M. SEIDEL, Institut für Organische Chemie der Universität Munchen, Germany.

T. T. VASSILYEVA, Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

G. WALLBILLICH, Institut für Organische Chemie der Universität Munchen, Germany.

R. W. WHITE, Rohm & Haas Co., Research Laboratory, Philadelphia 37, Pennsylvania, U.S.A.

VO
1
19

Tetrahedron, 1962, Vol. 17, p. 1. Pergamon Press Ltd. Printed in Northern Ireland

VOL.
17
1962

FOREWORD

THE papers collected in this Symposium Issue are devoted to new reactions and new classes of organic compounds. This general area of chemistry, while certainly not neglected in the past, has received added impetus in recent years. As will be seen in the accompanying papers, this progress has been aided by an increased understanding of reaction mechanisms and the appearance of new chemical tools. However, the unglamorous test-tube and unbridled imagination remain the organic chemist's mainstay.

The writer wishes to thank those who so generously contributed their work to this issue.

M. F. HAWTHORNE

Tetrahedron, 1962, Vol. 17, pp. 3 to 29. Pergamon Press. Ltd. Printed in Northern Ireland

DIPHENYL-NITRILIMIN UND SEINE 1.3-DIPOLAREN ADDITIONEN AN ALKENE UND ALKINE*

ROLF HUISGEN, MICHAEL SEIDEL,[1] GÜNTER WALLBILLICH[2] und HANS KNUPFER[3]
Institut für Organische Chemie der Universität München

VOL. 17 1962

(*Received* 23 *January* 1961)

Zusammenfassung—Das noch nicht bekannte Diphenyl-nitrilimin wird durch N_2-Abspaltung aus 2.5-Diphenyl-tetrazol bei 160° oder aus Benz-phenylhydrazid-chlorid mit Triäthylamin bei 20–80° bereitet. Es lagert sich *in situ* an Alkene und Alkine unter Bildung von 1.3-Diphenyl-Δ^2-pyrazolinen bzw. 1.3-Diphenyl-pyrazolen an. Die Addukte an 34 Alkene (normale Olefine, gespannte Doppelbindungen, Ketene, Diene, phenylkonjugierte Alkene, α,β-ungesättigte Carbonylverbindungen und Chinone) sowie 6 Alkine werden konstitutionell geklärt. Mit dem Nachweis der *cis*-Addition und der Ermittlung der Orientierungsregeln werden Beiträge zum Chemismus der 1.3-Dipolaren Addition geliefert. Die Additionsrichtung scheint von sterischen Faktoren stärker bestimmt zu werden als von polaren Substituenteneffekten.

Abstract—The hitherto undescribed diphenylnitrilimine is available by elimination of N_2 from 2.5-diphenyltetrazole at 160° or by dehydrochlorination of benzphenylhydrazide chloride at 20–80° with triethylamine. Diphenylnitrilimine adds *in situ* to alkenes and alkynes forming 1.3-diphenyl-Δ^2-pyrazolines and 1.3-diphenylpyrazoles, respectively. The structures of the adducts of 34 alkenes (normal olefins, strained double bonds, ketenes, dienes, phenylconjugated alkenes, α,β-unsaturated carbonyl compounds and quinones) and of 6 alkynes are elucidated. Proof of *cis*-addition and the determination of the orientation rules represent contributions to the mechanism of 1.3-dipolar addition. The direction of addition seems to be influenced more strongly by steric than by electronic factors.

A. 1.3-DIPOLARE ADDITIONEN UND NITRILIMINE

IN den letzten 3 Jahren wurde die 1.3-*Dipolare Addition* als in weiten Grenzen verallgemeinerbare Reaktion hinsichtlich Mechanismus und präparativ-synthetischer Bedeutung untersucht; jüngst wurde darüber in Vorträgen zusammenfassend berichtet.[4] Als 1.3-Dipol sei eine Verbindung a-b-c definiert, die am positiven Ladungszentrum a ein Elektronensextett besitzt und am anionischen Zentrum c über ein freies Elektronenpaar verfügt. Dieser 1.3-*Dipol* kann sich in einem Mehrzentrenprozess mit einem Mehrfachbindungssystem d-e, dem sog. *Dipolarophil*, unter cyclischer Elektronenverschiebung zu einem fünfgliedrigen Ring vereinigen, wobei die Formalladungen gelöscht werden.

Der 1.3-Dipol—wir beschränken uns hier auf den sogar weniger häufigen Typ, der im "ausgefalteten" Zustand I eine Doppelbindung trägt—ist nur dann eine stabile Verbindung, wenn ein freies Elektronenpaar am mittleren Atom b eine Mesomerie mit einer All-Oktett-Grenzformel II ermöglicht.

Wenn a und b ein Kohlenstoff- bzw. Stickstoffatom sind, haben wir die Klasse der

* I. Mitt. über 1.3-Dipolare Additionen.

[1] Aus der Dissertation M. Seidel, Universität München, 1960.
[2] Aus der Diplomarbeit G. Wallbillich, Universität München, 1959.
[3] Aus der Diplomarbeit H. Knupfer, Universität München, 1960.
[4] R. Huisgen, *Theoretische Chemie und Organische Synthese*. Vortrag bei der Zehnjahresfeier des Fonds der Chemischen Industrie, Düsseldorf, (1960); R. Huisgen, *Proc. Chem. Soc.* im Druck.

I II

Nitrilium-betaine vor uns; als anionische Endgruppe c kommen innerhalb der ersten Periode Kohlenstoff, Stickstoff und Sauerstoff in Frage. Das erste der sich so ergebenden drei Systeme ist das der Nitril-ylide III, die kürzlich zugänglich gemacht und 1.3-Dipolaren Additionen zugeführt wurden.[5] Das dritte enthält die seit fast 70 Jahren bekannten Nitriloxyde IV.[6] Vom zweiten System, den Nitril-iminen, soll im folgenden die Rede sein.

III IV V

Das Grundglied der Reihe, das sog. *Isodiazomethan* (V), war das einzige beschriebene Nitrilimin; es wurde von Müller durch Hydrolyse des explosiven Diazomethyllithiums erhalten.[7] Die Synthese eignet sich nur zur Bereitung bescheidener Mengen und versagt schon beim nächsten Glied, dem Isodiazoäthan.[8] Auf zwei Wegen haben wir inzwischen eine Vielfalt von aromatisch und aliphatisch substituierten Derivaten dargestellt. Deren enge reaktive Beziehung zu den Nitrilium-betainen III und IV scheint uns die Umtaufe der "Isodiazoverbindungen" in *Nitril-imine* zu rechtfertigen.

Da sich V unter Alkalikatalyse weitgehend in Diazomethan umlagert, ist V das energiereichere Isomere. Im Gegensatz zu den isolierbaren und leidlich stabilen Diazoalkanen vermochten wir die aryl- oder alkylsubstituierten Nitrilimine nicht in Substanz zu fassen. Die chemischen Eigenschaften wurden mittels Reaktionen *in situ* studiert. Die Nitrilimine zeigen in der 1.3-Dipolaren Addition ein breites Band von Möglichkeiten. Neben den hier beschriebenen Alkenen und Alkinen fanden wir auch *Mehrfachbindungssysteme mit Heteroatom* als Dipolarophile geeignet: Nitrile, Azomethine, Isocyanate, Senföle, Aldehyde und Thioketone[1–3]. Die Beschränkung auf das Diphenyl-nitrilimin als den meistuntersuchten Vertreter soll im folgenden die Übersicht erleichtern.

B. WEGE ZUM DIPHENYL-NITRILIMIN UND ANLAGERUNG AN GESPANNTE DOPPELBINDUNGEN

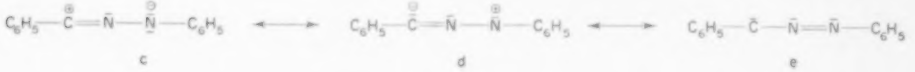
Bei 150–160° bricht der aromatische Kern des 2.5-*Diphenyltetrazols* (VI) auf; unter Abgabe von N_2 entsteht das Diphenylnitrilimin VII,[9] das sich leicht mit Verbindungen HX vereinigt; als HX vermögen Amine, Alkohole, Phenole, Thiophenole und Carbonsäuren zu fungieren.[10]

[5] R. Huisgen, H. Stangl und H. J. Sturm, unveröffentl.; kurze Erwähnung l.c.[4]
[6] A. Werner und H. Buss, *Ber. Dtsch. Chem. Ges.* **27**, 2193 (1894).
[7] E. Müller und W. Kreutzmann, *Liebigs Ann.* **512**, 264 (1934); E. Müller und D. Ludsteck, *Chem. Ber.* **87**, 1887 (1954); **88**, 921 (1955).
[8] E. Müller und W. Rundel, *Chem. Ber.* **89**, 1065 (1956).
[9] Vorläuf. Mitt.: R. Huisgen, M. Seidel, J. Sauer, J. W. McFarland und G. Wallbillich, *J. Org. Chem.* **24**, 892 (1959); R. Huisgen, *Angew. Chem.* **72**, 359 (1960).
[10] R. Huisgen und M. Seidel, *Chem. Ber.* **94**, im Druck (1961).

VI VII

Die zwei All-Oktett-Grenzformeln VII a und b bestimmen wohl am stärksten den Grundzustand des Diphenylnitrilimins. Drei weitere Grenzformeln (VII, c-e) besitzen je ein Elektronensextett, sind also energiereicher. Das Azocarben VIIe ist die einzige Struktur ohne Formalladungen. Hinzu kommen natürlich Grenzformeln, in denen die

a b



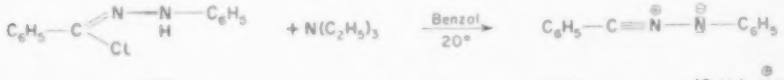
c d e

VII

Substituenten eine oder beide Formalladungen übernommen haben. Bei den HX-Additionen sucht die nucleophile Gruppe immer den Kohlenstoff von VI auf; Formel VIIc vermag daher als Symbol der Reaktivität zu dienen.*

Beim Zerfall des 2.5-Diphenyl-tetrazols in *Dicyclopentadien* bei 160° (Arbeitsweise A) lagerte sich VII an die Doppelbindung des Brückenringsystems an, wobei ein kristallines 1:1-Addukt X in einer Ausbeute von 68% (bezogen auf VI) erhalten wurde. Die Doppelbindung des Bicyclo-[2.2.1]-hept-2-en-Systems ist bekanntlich *winkelgespannt*[11] und zeigt ihre hohe Additionsbereitschaft u.a. gegenüber Phenylazid;[12] diese Bildung von Triazolinen bietet ebenfalls ein Beispiel für 1.3-Dipolare Additionen.

Die relativ hohe Temperatur der Freisetzung des Diphenylnitrilimins aus VI erlegt Beschränkungen in der Auswahl der Dipolarophilen auf. Solche mit Siedepunkt unter 160° lassen sich allenfalls im Druckgefäss umsetzen; die Stabilität des Dipolarophils bei dieser Temperatur ist stets Voraussetzung. In der Reaktion des *Benzphenylhydrazid-chlorids* VIII mit Triäthylamin in Benzol bei Raumtemperatur fanden wir eine ergiebige Quelle für VII, die frei von den obenerwähnten Nachteilen ist. In Gegenwart von 4.6 Äquival. Dicyclopentadien isolierten wir das gleiche 1:1-Addukt X in 83% Ausbeute. Die Abscheidung des Triäthylammonium-chlorids setzte wenige Sekunden nach Zugabe des Triäthylamins ein und war nach einigen Stunden abgeschlossen.



VIII VII

Die Resultate mit einigen weiteren Bicyclo-[2.2.1]-hepten-Derivaten als Dipolarophilen finden sich in Tabelle 1. Hier wie in den meisten Versuchen der Tabellen 2–5

* Wir wählen den Begriff "Symbol", um der unzulässigen Gleichsetzung einer mesomeren Grenzformel mit einer Reaktionsformel vorzubeugen.

[11] Die Hydrierungswärme des Bicyclo-[2.2.1]-heptens ist um 6 kcal höher als die des Cyclohexens und übertrifft die des Cycloheptens gar um 7 kcal: R. B. Turner, W. R. Meador und R. E. Winkler, *J. Amer. Chem. Soc.* **79**, 4116 (1957).

[12] K. Alder, G. Stein und H. Finzenhagen, *Liebigs Ann.* **485**, 211 (1931); K. Alder, G. Stein und W. Friedrichsen, *Ibid.* **501**, 1 (1933).

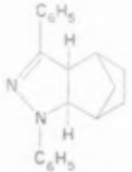
wurde VIII mit 2–5 Äquival. des Dipolarophils und ca. 4 Äquival. Triäthylamin in Benzol behandelt (Arbeitsweise B). In einigen Fällen wurden auch mit geringerem oder ohne Dipolarophil-Überschuss befriedigende Ergebnisse erzielt. Weniger aktive Dipolarophile werden zweckmässig in grösserem Überschuss bzw. als Lösungsmittel verwendet. Die meisten Additionen erfolgten glatt bei Raumtemperatur; jedoch waren in siedendem Benzol zuweilen die Ausbeuten etwas höher. Langsames Eintropfen des Triäthylamins, d.h. also Arbeiten mit geringer Stationärkonzentration des 1.3-Dipols, erübrigt sich bei ausreichend aktiven Dipolarophilen.

TABELLE 1. ADDITIONEN DES DIPHENYL-NITRILIMINS AN BICYCLO-[2.2.1]-HEPT-2-EN UND DERIVATE

Arbeitsweise A: Thermolyse des 2.5-Diphenyl-tetrazols im Dipolarophil; Arbeitsweise B: Umsetzung mit Benz-phenylhydrazid-chlorid und Triäthylamin in Benzol

Dipolarophil	Arbeitsweise und Temp.	Addukt		
		Ausbeute % d.Th.	Formel	Schmp.
Bicyclo-[2.2.1]-hept-2-en	B, 20°	85	IX	171–172°
Bicyclo-[2.2.1]-hept-2-en	B, 80°	94	IX	171–172°
α-Dicyclopentadien	A, 160°	68	X	173–174°
α-Dicyclopentadien	B, 20°	83	X	175–176°
α-Dicyclopentadien	B, 80°	87	X	175–176°
Bicyclo-[2.2.1]-hepta-2.5-dien	B, 65°	79	XIII	133–135°
		+ 6	XIV	~320°
endo-cis-Bicyclo-[2.2.1]-hept-5-en-dicarbonsäure-(2.3)-anhydrid	B, 80°	55	XV	279–281°

Nur im Fall des *Bicyclo*-[2.2.1]-*heptens* wurden die Bedingungen der Arbeitsweise B variiert; die maximale Ausbeute an IX betrug 94%. Tetrahydrofuran als Solvens war mit 81% Addukt-Ausbeute bei 20° dem Benzol etwa gleichwertig. Schütteln der benzolischen Lösung von Norbornen und VIII mit wässriger Kalilauge bei 20° gab 76% d.Th. IX; das Arbeiten im zweiphasigen System bietet aber keine Vorteile. Viele der 1.3-Additionen der Tabellen 1–5 wurden nur einmal ausgeführt und dürften in den Ausbeuten noch zu verbessern sein.



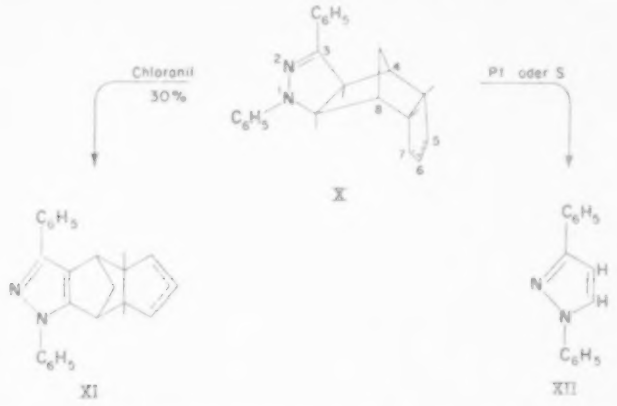
IX

Die hellgelbe Farbe des kristallisierten Bicyclo-[2.2.1]-hept-2-en-Addukts IX, die UV-Absorption und die intensive blaugrüne Fluoreszenz[13] seiner Lösungen sowie die Farbreaktion mit Salpetersäure in konz. Schwefelsäure[14] sind charakteristisch für 1.3-*Diaryl*-Δ^2-*pyrazoline*. Brom in Chloroform wirkt nicht dehydrierend, sondern substituiert lediglich die p-Position des N-gebundenen Phenyls in IX.

[13] F. Straus, *Ber. Dtsch. Chem. Ges.* **51**, 1457 (1918); O. Neunhoeffer und D. Rosahl, *Chem. Ber.* **86**, 226 (1953); *Z. Elektrochem., Ber. Bunsenges. Physik. Chem.* **57**, 81 (1953).

[14] L. Knorr, *Ber. Dtsch. Chem. Ges.* **26**, 100 (1893).

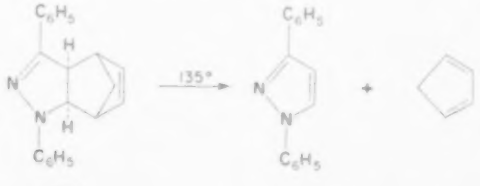
Beim α-*Dicyclopentadien* ist angesichts der Möglichkeit von Struktur- und Stereoisomerie die bis zu 87% betragende Ausbeute am einheitlichen 1:1-Addukt bemerkenswert. Am Bicyclo-[2.2.1]-hepten-Gerüst verlaufen alle Diensynthesen[15] nach *exo-cis*. Auch für die Anlagerung des Phenylazids konnten Alder *et al.*[16] den gleichen sterisch einheitlichen Ablauf wahrscheinlich machen. Aus Analogiegründen formulieren wir das Diphenyl-nitrilimin-Addukt gemäss X als *exo-cis*-Verbindung. Durch Strichelung wurde in X gekennzeichnet, dass sich die CC-Doppelbindung in 5·6 oder 6·7 befinden kann. Da ein richtender Einfluss dieser Doppelbindung des α-Dicyclopentadiens auf die 1.3-Addition schwer erkennbar ist, überrascht deren strukturell einheitlicher Verlauf. Auch die Möglichkeit einer isomorphen Vertretbarkeit der beiden Doppelbindungsisomeren im Kristall muss erwogen werden.



X XI XII

Die Aromatisierung des Pyrazolinringes in X gelang mit Chloranil in siedendem Xylol. Die Umwandlung von sp^3 in sp^2-Zentren in den Positionen 3a und 8a muss mit Anwachsen der Winkelspannung (Norbornen-System) erkauft werden, was sich in geringer Dehydrierungsgeschwindigkeit und mässiger Ausbeute an XI äussert. Die enge Beziehung der U.V.-Absorptionsspektren von X und XI zu denen von authent. 1.3-Diphenyl-Δ^2-pyrazolin und 1.3-Diphenyl-pyrazol (Fig. 1) sichert die vorgeschlagenen Konstitutionen.

Bei der Behandlung von X mit Platinkohle bei 300° oder mit Schwefel bei 200–250° war die Dehydrierung des Pyrazolinringes verknüpft mit einer Absprengung des alicyclischen Molekülteils; bis zu 46% 1.3-Diphenyl-pyrazol (XII) wurden erhalten, während das zweite Spaltstück nicht isolierbar war.



XIII

[15] S. B. Soloway, *J. Amer. Chem. Soc.* **74**, 1027 (1952); J. K. Stille und D. A. Frey, *Ibid.* **81**, 4273 (1959); K. Alder, J. Mönch und H. Wirtz, *Liebigs Ann.* **627**, 47 (1959).
[16] K. Alder, G. Stein und S. Schneider, *Liebigs Ann.* **515**, 185 (1935).

Obwohl bei der Anlagerung von VII an *Bicycloheptadien* mit 12 Moläquival. des Dipolarophils gearbeitet wurde, liessen sich neben 79% des 1:1-Addukts XIII noch 6% eines Diaddukts, vermutlich XIV, fassen. Die hellgelben Kristalle von XIII erleiden schon beim Schmelzpunkt (133–135°) einen Retrodien-Zerfall, der bei der präparativen Durchführung 98% 1.3-Diphenyl-pyrazol und 77% Cyclopentadien ergab.

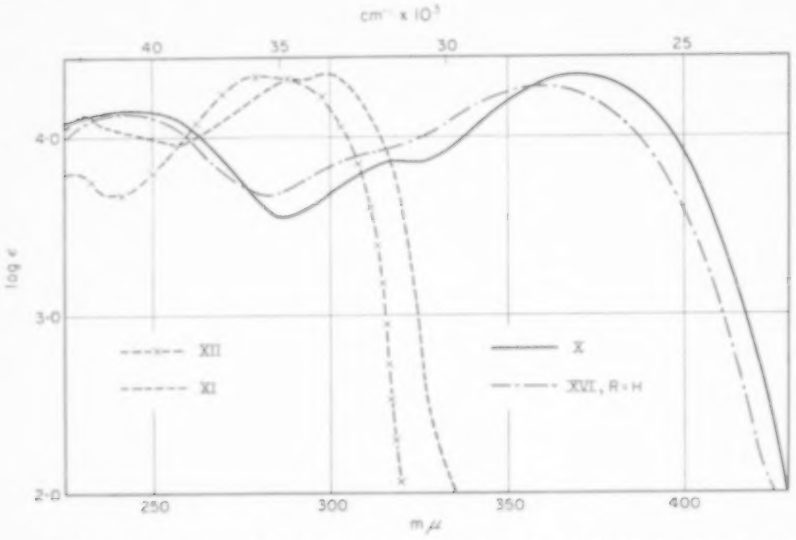
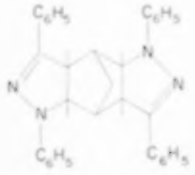
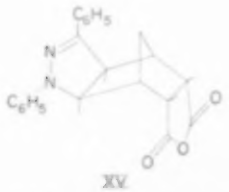


FIG. 1.—U.V.-Absorption von 1.3-Diphenyl-4.8-methano-3a.4.4a.7a.8.8a-hexahydro-indeno-[5.6-c]-pyrazol (X), 1.3-Diphenyl-4.8-methano-4.4a.7a.8-tetrahydro-indeno-[5.6-c]-pyrazol (XI), 1.3-Diphenyl-Δ^2-pyrazolin (XVI, R = H) und 1.3-Diphenyl-pyrazol (XII) in Chloroform.



XIV



XV

Die grünblaue Fluoreszenz des Diaddukts weist auf die 1.3-Diphenyl-Δ^2-pyrazolin-Struktur; die Extinktion der U.V.-Maxima zeigt die Anwesenheit von 2 derartigen Ringen. Neben XIV kommt noch eine Möglichkeit mit anderer relativer Orientierung der Heteroringe in Frage.

Das Addukt aus Cyclopentadien und Maleinsäureanhydrid lagerte VII an unter Bildung des Pyrazolins XV.

C. NICHTKONJUGIERTE OLEFINE, DIPHENYLKETEN UND KETENACETAL

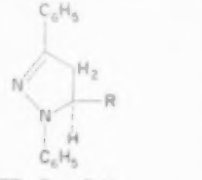
Die dipolarophile Aktivität der normalen unkonjugierten Doppelbindung (Tabelle 2) ist relativ gering. Unter den offenkettigen Olefinen treten die monosubstituierten Äthylene anscheinend am leichtesten in Reaktion. Weitere Versuche müssen die Grenzen abstecken.

TABELLE 2. ADDITIONEN DES DIPHENYL-NITRILIMINS AN NICHTKONJUGIERTE ALKENE, DIPHENYLKETEN UND KETENACETAL

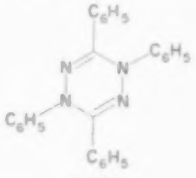
Dipolarophil	Arbeitsweise und Temp.	Addukt		
		Ausbeute % d.Th.	Formel	Schmp.
n-Hepten-(1)	B*, 90°	85	XVI	56–58°
Undecylensäure-äthylester	B*, 90°	80	XVII	40–42°
Cyclopenten	B, 80°	78	XIX	137·5–139°
Cyclohexen	B, 80°	0		
Diphenylketen	B, 80°	24	XX	160–162°
Keten-diäthylacetal	B, 80°	79	XXI	67–69°

* In Dipolarophil als Lösungsmittel.

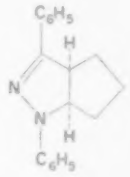
Die Bildung von XVI und XVII aus *Hepten-(1)* bzw. *Undecylensäureester* vollzog sich recht glatt, wenn man eine hohe Konzentration des Dipolarophils verwendete. Beim Arbeiten mit nur 3 Moläquival. des Undecylensäureesters in Benzol traten neben XVII noch 28% 1.3.4.6-Tetraphenyl-1.4-dihydro-1.2.4.5-tetrazin (XVIII) als Ergebnis einer Kopf-Schwanz-Dimerisation von VII auf. Das Erscheinen dieses Produkts zeigt jeweils die mangelnde Aktivität des Dipolarophils an.



XVI $R = nC_5H_{11}$
XVII $R = (CH_2)_8CO_2C_2H_5$



XVIII

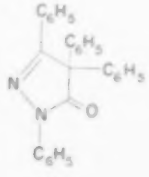


XIX

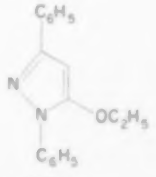
Die Stellung des aliphatischen Substituenten wurde am Beispiel XVI durch Oxydation ermittelt. Bezüglich der Orientierung bei der Anlagerung von VII an das monosubstituierte Äthylen sei auf die späteren Ausführungen verwiesen (S. 15).

Unter den Cycloolefinen lieferte das *Cyclopenten* mit VIII und Triäthylamin in siedendem Benzol 78% des Adduktes XIX, während mit *Cyclohexen* keine Pyrazolinbildung nachweisbar war. Das U.V.-Spektrum von XIX ist nahezu identisch mit dem des Norbornen-Adduktes IX. Die Überlegenheit des Cyclopentens vor Cyclohexen als Dipolarophil beobachteten wir auch beim Arbeiten mit anderen 1.3-Dipolen.

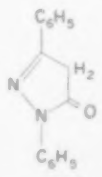
Die Umsetzung von VII mit *Diphenylketen* führte zu einem uneinheitlichen Produkt. Eine zu 24% gefasste Komponente zeigt die Analysenwerte des Monoadduks; die Formulierung als 1.3.4.4-Tetraphenyl-Δ^2-pyrazolon-(5) (XX) bedarf noch der Bestätigung.



XX



XXI



XXII

Die Konjugation der Doppelbindung mit zwei O-Funktionen macht das *Ketendiäthylacetal* zu einem wirksamen Dipolarophil. Das farblose Produkt zeigt die im Vergleich mit den Pyrazolinen wesentlich kurzwelligere Absorption der Pyrazole. Laut Elementaranalyse hat das Primäraddukt Alkohol abgespalten; ob diese Aromatisierung unmittelbar auf die 1.3-Addition folgt oder erst bei der Aufarbeitung durch Hochvakuum-Destillation eintritt, sei dahingestellt. Dass es sich um 1.3-Diphenyl-5-äthoxy-pyrazol (XXI) handelt, wurde durch die energische salzsaure Hydrolyse zu XXII bewiesen; das 1.3-Diphenyl-Δ^2-pyrazolon-(5) war mit einem authent. Präparat[17] identisch.

Die Orientierung bei der Addition von VII an Diphenylketen und Keten-diäthylacetal ist die erwartete, wenn wir wieder die Grenzformel VIIc mit Carbonium-Kohlenstoff und anionischem Stickstoff als Symbol betrachten.

D. KONJUGIERTE ALKENE

Jegliche Art von Konjugation steigert die Aktivität eines Olefins als Dipolarophil. Das gilt nicht nur für die Anlagerung von VII, sondern offensichtlich für alle 1.3-Dipolaren Additionen, wie quantitative Aktivitätsvergleiche gegenüber einer Reihe von 1.3-Dipolen lehren. Da die Konjugationsenergie des Alkens im Zuge der Addition—die sp^2-Zentren werden in tetraedrische umgewandelt—geopfert werden muss, ist die Reaktionsenthalpie geringer als bei der Addition an eine isolierte Doppelbindung. Dennoch erniedrigt die Konjugation den Aktivierungsaufwand; das entspricht sich überkreuzenden Energieprofilen für die 1.3-Dipolaren Additionen an konjugierte und nichtkonjugierte Alkene.

Wie kann die Konjugation die Aktivierungsenergie vermindern? Die naheliegendste Deutung bietet die *Stabilisierung von Partialladungen im Übergangszustand* der 1.3-Dipolaren Addition. Synchroner Ablauf im Schema von S. 4 bedeutet nicht, dass im Übergangszustand die Schliessung der beiden neuen Bindungen prozentual gleich weit fortgeschritten sein muss. Bei ungleicher Bindungsschliessung muss notwendig auf *einem* Kohlenstoffatom des Dipolarophils in der Aktivierungskonfiguration eine Partialladung auftreten; diese kann nun von eventuellen in Konjugation befindlichen Substituenten übernommen werden. Unter diesem Gesichtspunkt seien die Orientierungsphänomene bei der Addition an konjugierte Systeme betrachtet (Tabelle 3).

Das in hoher Ausbeute isolierte Monoaddukt des *Butadiens* zeigt Pyrazolin-Spektrum und -Fluoreszenz. Das Dien kann VII zu zwei strukturell verschiedenen Addukten in 1.2- aufnehmen, von denen aber nur eines gebildet wird. Da eine benachbarte Doppelbindung leichter eine positive als eine negative Ladung durch Resonanz zu stabilisieren vermag, war eine Anlagerung des Nitrilimin-Kohlenstoffs an das C-1 des Butadiens gemäss XXIII zu erwarten. Diese Konstitution liess sich durch die Chloranil-Dehydrierung zum 1.3-Diphenyl-5-vinyl-pyrazol (XXIV) und dessen Oxydation zur 5-Carbonsäure (XXV) bestätigen. Die noch nicht beschriebene Säure XXV wurde zum Vergleich aus dem konstitutionell gesicherten 1.3-Diphenyl-5-methyl-pyrazol[18] durch Permanganat-Oxydation bereitet.

Da *Cyclopentadien* rasch di- und trimerisiert, war die Bildung von Nebenprodukten bei der Anlagerung von VII nicht zu vermeiden. Die Ausbeute der Tabelle 3 bezieht sich auf einen Versuch mit 1.5 Moläquival. Cyclopentadien. Die katalytische

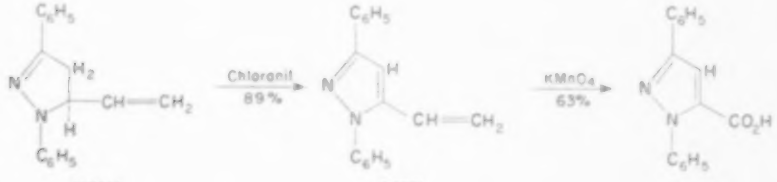
[17] L. Knorr und C. Klotz, *Ber. Dtsch. Chem. Ges.* **20**, 2545 (1887).
[18] K. v. Auwers und H. Mauss, *Ber. Dtsch. Chem. Ges.* **59**, 611 (1926).

VOL. 17 1962

TABELLE 3. ADDITIONEN DES DIPHENYL-NITRILIMINS AN KONJUGIERTE ALKENE

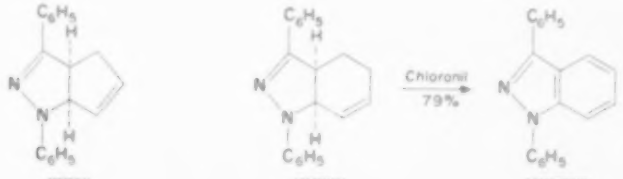
Dipolarophil	Arbeitsweise und Temp.	Addukt		
		Ausb. % d.Th.	Formel	Schmp.
Butadien	B, 20°	94	XXIII	76–77·5°
Cyclopentadien	B, 20°	58	XXVI	183–184°
Cyclohexa-1.3-dien	B, 80°	73	XXVII	119·5–121°
Styrol	B, 60°	88	XXIX	137–138°
1.2-Dihydronaphthalin	A, 160°	84	XXX	143–149°
1.2-Dihydronaphthalin	B, 80°	75	XXX	151–152°
Inden	B, 80°	78	—	171–172°
trans-Stilben	B, 80°	86	XXXIII	166·5–168°
cis-Stilben	B,* 50°	53	XXXIV	194·5–195·5°
Acenaphthylen	B, 80°	90	XXXVI	255·5–257°
Dibenzo-[b.f]-azepin	B, 80°	55	XXXVII	264–265·5°

* Ohne Lösungsmittel.



XXIII XXIV XXV

Hydrierung von XXVI ergab das Cyclopenten-Addukt XIX. Die Bromsubstitution in der p-Stellung des 1-Phenyls verläuft rascher als die Bromaddition an die CC-Doppelbindung in XXVI. Die Lage eben dieser Doppelbindung wurde in Analogie zu XXIII formuliert.



XXVI XXVII XXVIII

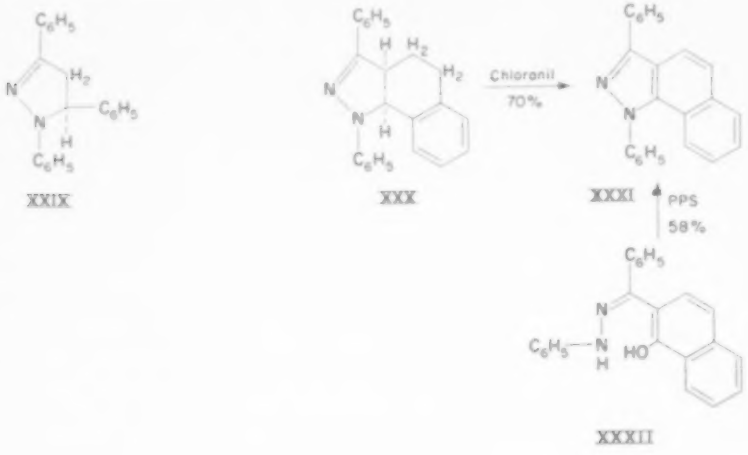
Dass es sich bei dem hellgrüngelben Addukt XXVII aus *Cyclohexa*-1.3-*dien* um einen Abkömmling des Tetrahydroindazols handelt, wurde durch die Dehydrierung zum 1.3-Diphenyl-indazol (XXVIII)[19] dargetan.

Styrol als einfachstes phenylkonjugiertes Alken vereinigte sich mit VII zu 88% 1.3.5-Triphenyl-Δ^2-pyrazolin (XXIX), identisch mit einem authent. Präparat.[20] Die Additionsrichtung entspricht der des Butadiens.

Während 1.2-*Dihydronaphthalin* mit Benz-phenylhydrazid-chlorid/Triäthylamin in siedendem Benzol das leicht zu reinigende Addukt XXX lieferte, ergab die Zersetzung des Diphenyl-tetrazols in 1.2-Dihydronaphthalin bei 160° in hoher Ausbeute ein

[19] W. Borsche und W. Scriba, *Liebigs Ann.* **540**, 83 (1939).
[20] L. Knorr und H. Laubmann, *Ber. Dtsch. Chem. Ges.* **21**, 1205 (1888).

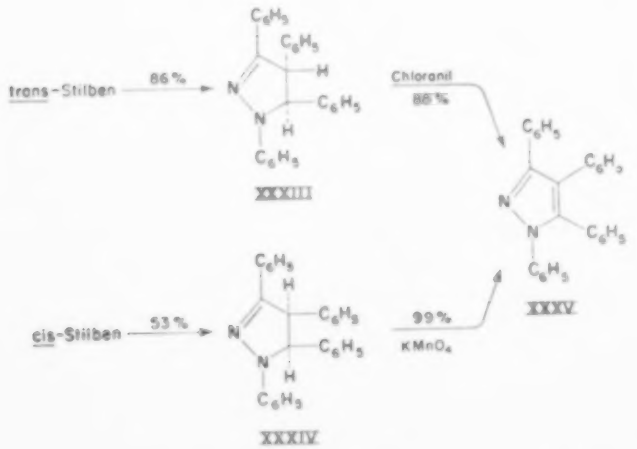
Isomerengemisch, das XXX als Hauptkomponente enthielt, Wir vermuten, dass bei der höheren Temperatur auch die zweite Additionsrichtung zum Zug kommt.



XXIX XXX XXXI XXXII

Bei XXX bleibt auffallenderweise die charakteristische Fluoreszenz der 1.3-Diaryl-Δ^2-pyrazoline aus; vermutlich verhindert der ankondensierte Benzolkern die notwendige Koplanarität des N-Phenyl-pyrazolinsystems. Das aus der durchgreifenden Chloranil-Dehydrierung hervorgehende 1.3-Diphenyl-6.7-benzo-indazol (XXXI) wurde auf eindeutigem Weg synthetisiert: Cyclisierende Dehydratisierung des Phenylhydrazons des 2-Benzoyl-1-hydroxy-naphthalins (XXXII) mit Polyphosphorsäure bei 100°. Das einheitliche *Inden-Addukt* ist wohl analog XXX zu formulieren (mit CH_2 statt CH_2—CH_2).

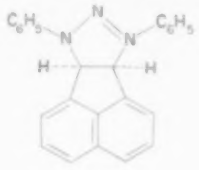
Wie die verwandte Diels–Alder-Reaktion sollte auch die 1.3-Dipolare Addition als Mehrzentrenprozess einen *cis*-Ablauf zeigen. Zum Nachweis eignen sich vor allem *cis-trans*–isomere Alkene als Dipolarophile. Tatsächlich gelangten wir, von trans- und cis-*Stilben* ausgehend, zu den diastereomeren Diphenyl-nitrilimin-Addukten XXXIII



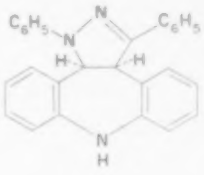
XXXIII XXXV XXXIV

und XXXIV; in den Mutterlaugen vermochten wir nicht das jeweils andere Diastereomere nachzuweisen. Beide Pyrazoline liessen sich zu ein und demselben 1.3.4.5-Tetraphenyl-pyrazol (XXXV) dehydrieren. Während dies bei der *cis*-Verbindung XXXIV mit Permanganat in Aceton praktisch vollständig gelang, trat XXXIII unter gleichen Bedingungen nicht in Reaktion. Hier bedurfte es der Einwirkung von Chloranil in siedendem Xylol.

Die etwas winkelgespannte Doppelbindung des *Acenaphthylens* trat leicht in Reaktion und gab 90% XXXVI. Auch die in das cyclische 8π-System des *Dibenzo*-[b.f]-*azepins*[21] einbezogene Doppelbindung erwies sich als ausreichend aktiv; mit nur einem Moläquival. des Dipolarophils wurden 55% XXXVII erhalten.



XXXVI

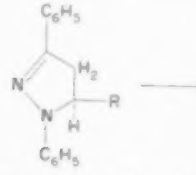


XXXVII

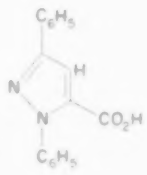
E. α,β-UNGESÄTTIGTE CARBONESTER UND NITRILE SOWIE CHINONE

Lagert sich schon Diphenyl-diazomethan leicht an α,β-ungesättigte Carbonylverbindungen an, so war dies erst recht von dem reaktionsfreudigeren Isomeren, dem Diphenyl-nitrilimin, zu erwarten. Die konstitutionelle Klärung der in Tabelle 4 aufgeführten Addukte erlaubt mechanistische Rückschlüsse.

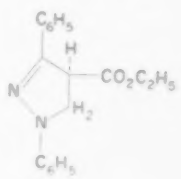
Die aus *Acrylester* und *Acrylnitril* in glatter Addition erhaltenen Pyrazoline XXXVIII und XXXIX wurden mit Chloranil in die Pyrazole übergeführt und lieferten beide bei der alkalischen Verseifung bzw. schwefelsauren Hydrolyse reine 1.3-Diphenyl-pyrazol-carbonsäure-(5) (XXV). Damit ist die Orientierung eindeutig festgelegt.



XXXVIII R = $CO_2C_2H_5$
XXXIX R = CN



XXV



XL

Die Grenzformel VIIc, die sich bislang als Symbol für die Diskussion des Additionssinns bewährte, liess erwarten, dass die nucleophile N-Funktion in die β-Position des Acrylsäureesters gemäss XL eintritt. Der ausschliesslich beschrittene Reaktionsweg zeigt die *umgekehrte* Orientierung. Dieses Versagen überzeugt von der Notwendigkeit, andere orientierende Effekte zu suchen.

Die Betrachtung der All-Oktett-Grenzformeln VIIa und b lehrt, dass das Nitrilimin über 2 nucleophile Zentren verfügt. Es ist allerdings schwer vorauszusehen, wie weit

[21] R. Huisgen, E. Laschtuvka und F. Bayerlein, *Chem. Ber.* **93**, 392 (1960).

TABELLE 4. ADDITIONEN DES DIPHENYL-NITRILIMINS AN α,β-UNGESÄTTIGTE CARBONYLVERBINDUNGEN UND NITRILE

Dipolarophil	Arbeitsweise und Temp.	Addukt		
		Ausb. % d.Th.	Formel	Schmp.
Acrylsäure-äthylester	B, 20°	85	XXXVIII	99–101°
Acrylnitril	B, 20°	85	XXXIX	138–140°
Crotonsäure-äthylester	B, 80°	95	—	fl.
Zimtsäure-äthylester	B, 80°	83	—	121·5–124·5°
Zimtsäure-äthylester	A, 160°	86	XLI	113–116°
Acetessigsäure-äthylester	A, 165°	67	XLII	102–104°
O-Äthyl-acetessigester	A, 165°	19	XLII	102–104°
O-Acetyl-acetessigester	A, 165°	62	XLII	102–104°
Maleinsäureanhydrid	A,* 155°	37	XLIII	190–192°
Maleinsäureanhydrid	A, 165°	35	XII	82–84°
Fumarsäure-dimethylester	B, 80°	99	XLIV	149·5–151°
Fumarsäure-dimethylester	A, 165°	88	XLIV	148–150°
Maleinsäure-dimethylester	B, 80°	93	XLIV	149·5–151°
Maleinsäure-dimethylester	A, 165°	51	XLIV	149–150°
		+4	XLV	141–143°
Dimethyl-maleinsäure-anhydrid	A,* 155°	55	XLVI	133–134°
Dimethyl-fumarsäure-dimethylester	B,** 50°	74	XLVII	107·5–108·5°
Dimethyl-maleinsäure-dimethylester	B,** 50°	33	XLVIII	144–145°
α-Naphthochinon	A, 165°	85	XLIX	257–259°
2-Methyl-α-naphthochinon	A,* 155°	33	L	245–247°

* Anisol als Solvens; ** ohne Lösungsmittel.

die Mesomerie dieser Grenzformeln infolge ihrer *unterschiedlichen Geometrie* sterisch behindert sein wird. Energetische Erwägungen sowie eine Betrachtung der molecular

VII a

VII b

orbitals* lassen uns vermuten, dass VIIa mit grösserem Gewicht am Grundzustand beteiligt ist und dessen Geometrie vornehmlich bestimmt. Dennoch entspricht die Molekel bezüglich der Ladungsverteilung mehr einem linearen "Tripol" als dem Zwitterion VIIa. Der Stickstoff ist also nicht *eindeutig* als nucleophile Komponente prädestiniert. Der Vorzug einer Reaktion des 1.3-Dipols gemäss Symbol VIIc ist umso geringer, als man bei einer cyclischen Bindungsverschiebung (Schema von S. 4) nicht einmal die Richtung der Elektronenbewegung angeben kann.

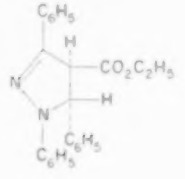
Welche zusätzlichen Effekte bestimmen nun die Orientierung? Mehrzentrenprozesse erfordern ein hohes Mass von Ordnung der Komponenten im Aktivierungsvorgang; sie sind gegenüber *sterischen Faktoren* notorisch empfindlich. Tatsächlich haben kinetische Studien der Diphenyldiazomethan-Addition an Alkene einen überraschend hohen Einfluss des Raumanspruchs des Dipolarophils an den Tag gebracht.[22]

* Herrn Prof. J. D. Roberts, Pasadena (U.S.A.), sei für hilfreiche Diskussionen aufrichtig gedankt.

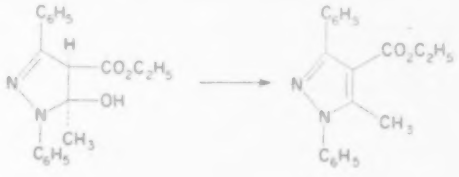
[22] Vgl. l.c.[4] sowie R. Huisgen, H. Stangl, H. J. Sturm und H. Wagenhofer, *Angew. Chem.* **73**, 170 (1961).

Wenn der Grundzustand des Diphenyl-nitrilimins der Struktur VIIa geometrisch nahesteht, dann ist der endständige Stickstoff räumlich freier zugänglich als der Kohlenstoff. 1-Substituierte oder 1.1-disubstituierte Äthylene sollten daher eine Orientierung sterisch bevorzugen, bei der das höhersubstituierte Zentrum vom Stickstoff in VII gebunden wird. Die Additionsrichtung bei den monosubstituierten Äthylenen (Tabelle 2) wird damit klar. Bei Butadien und Styrol operieren elektronische und sterische Faktoren in gleicher Richtung. Beim Acrylester scheint von den gegeneinander arbeitenden Einflüssen der sterische stärker zu sein. Allerdings selzt die Stärke des orientierenden Effekts in Erstaunen.

Sind Substituenten in 1- und 2-Stellung des Äthylens im Raumanspruch vergleichbar, dann sollten die polaren Effekte wieder die Orientierung festlegen. Mit *Crotonsäure-äthylester* und *Zimtsäure-äthylester* erhielten wir Isomerengemische, deren quantitative Trennung noch nicht gelang. Aus dem rohen Zimtester-Addukt waren nach Chloranil-Dehydrierung 50% d.Th. 1.3.5-Triphenyl-pyrazol-carbonsäure-(4)-äthylester isolierbar. Als Hauptprodukt lieferte Zimtester somit XLI, in welchem der Stickstoff von VII die elektrophile β-Position zur Carbonesterfunktion aufgesucht hat.



XLI



XLII

In der Enolform des *Acetessigesters* liegt ein trisubstituiertes Äthylen vor. Das Zentrum mit höherem Raumanspruch tritt ausschliesslich mit dem Stickstoff von VII in Bindungsbeziehung. Nach spontaner Wasserabspaltung lieferte das Primäraddukt nämlich den 1.3-Diphenyl-5-methyl-pyrazol-carbonsäure-(4)-äthylester (XLII)[23]. O-*Acetyl-* und O-*Äthyl-acetessigester* gingen unter Eliminierung von Essigsäure resp. Äthanol ebenfalls in XLII über. Sterischer und elektronischer Effekt bestimmen den Additionssinn hier in gleicher Richtung.

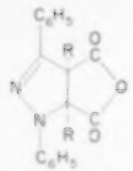
Schon Fusco und Mitarbeiter[24] bereiteten fünfgliedrige Heterocyclen durch Umsetzung von zahlreichen CH-aciden Verbindungen mit Hydrazidhalogeniden in alkoholischem Alkali. Die Formulierung der italienischen Autoren, die eine primäre Substitution des Halogens gegen das Anion der CH-aciden Verbindung vorsieht, mag zutreffen. In der letzten Arbeit der Reihe wiesen Fusco und Romani[25] auf die Möglichkeit einer primären HHal-Abspaltung zur "Isodiazoverbindung" hin.

Die Wechselwirkung zerfallenden Diphenyl-tetrazols mit *Maleinsäureanhydrid* in siedendem Anisol führte zum 1.3-Diphenyl-Δ^2-pyrazolin-*cis*-4.5-dicarbonsäureanhydrid (XLIII). Die mehr als ein Moläquival. betragende Gasentwicklung legte einen teilweisen Zerfall des Addukts nahe. Bei der Thermolyse von VI in überschüssigem Maleinanhydrid ohne Solvens liess sich nur noch 1.3-Diphenyl-pyrazol als Ergebnis einer CO- und CO_2-Abspaltung aus XLIII fassen.

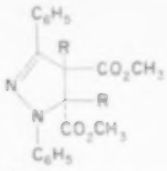
[23] G. Minunni und G. Lazzarini, *Atti Reale Accad. Naz. Lincei, Rend.* (5) **15 I**, 19 (1906).

[24] R. Fusco und R. Justoni, *Gazz. Chim. Ital.* **67**, 3 (1937); R. Justoni, *Ibid.* **68**, 49 (1938); R. Justoni und R. Fusco, *Ibid.* **68**, 59 (1938); R. Fusco und C. Musante, *Ibid.* **68**, 147, 665 (1938); R. Fusco, *Ibid.* **69**, 344, 353, 364 (1939); **72**, 411 (1942); R. Fusco und R. Romani, *Ibid.* **76**, 419, 439 (1946).

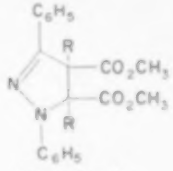
[25] R. Fusco und R. Romani, *Gazz. Chim. Ital.* **78**, 342 (1948).



XLIII R = H
XLVI R = CH_3



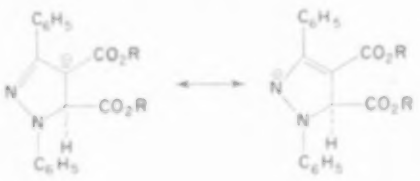
XLIV R = H
XLVII R = CH_3



XLV R = H
XLVIII R = CH_3

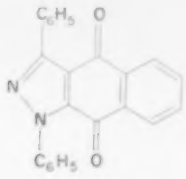
Obgleich es nicht statthaft ist, aus Ausbeuten auf absolute Reaktionsgeschwindigkeiten zu schliessen, sei auf die 99-proz. Adduktausbeute aus *Fumarsäure-dimethylester* und VIII + Triäthylamin hingewiesen. Auch die Thermolyse von VI in Fumarester ist mit 88% des gleichen blassgrüngelben Addukts XLIV besonders ergiebig. Die Einwirkung von Chloranil ermöglichte eine glatte Aromatisierung zum 1.3-Diphenyl-pyrazol-dicarbonsäure-(4.5)-dimethylester (LVI).

Dass *Maleinsäure-dimethylester* bei der Arbeitsweise B ebenfalls den *trans*-Dicarbonester XLIV lieferte, scheint zunächst der stereoselektiven *cis*-Addition zu widersprechen. Die Tetrazol-Pyrolyse bei 165° (Arbeitsweise A) ergab übrigens 4% *cis*-Dicarbonester XLV neben 51% XLIV. Die basenkatalysierte Epimerisierung XLV → XLIV —bei der Arbeitsweise B durch Triäthylamin, bei A vielleicht durch die geringe Eigenbasizität des Addukts— bietet eine zwanglose Erklärung. Nur die neutrale Hydrolyse des Anhydrids XLIII führte bei nachfolgender Veresterung mit Diazomethan zum *cis*-Diester XLV. Die Behandlung von XLIII mit Sodalösung genügt, um den Übergang in die stabilere *trans*-Reihe auszulösen. Die Epimerisierung dürfte wohl über ein mesomeriestabilisiertes Anion erfolgen:

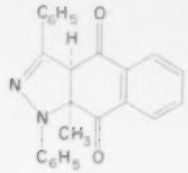


Die Verwendung eines tetrasubstituierten Äthylens als Dipolarophil erlaubt die nachträgliche Epimerisierung des Addukts nicht. In der Tat blieb die sterische Beziehung von *Dimethyl-fumarsäure-* und *-maleinsäure-dimethylester* in den Addukten gewahrt. Aus viel trägeren Umsetzungen resultierten die *trans-* und *cis*-Diester XLVII und XLVIII. Die *cis*-Verbindung XLVIII konnte auch aus dem Addukt des *Dimethyl-maleinsäureanhydrids* XLVI erhalten werden.

Die Reaktivität der Chinone schliesst sich eng an die der α,β-ungesättigten Ketone an. Aus der Thermolyse des Diphenyl-tetrazols in überschüssigem *α-Naphthochinon* ging zu 85% das gelbe Chinon XLIX hervor. Offensichtlich isomerisiert sich das primäre Pyrazolin-diketon bei 165° unter Protonenwanderung zum Pyrazol-hydrochinon. Da elektronenliefernde Substitution das Redoxpotential eines Chinons senkt, wurde das Pyrazol-hydrochinon durch überschüssiges α-Naphthochinon sofort zum 1.3-Diphenyl-4.9-dioxo-4.9-dihydro-naphtho-[2.3-c]-pyrazol (XLIX) dehydriert. Die Carbonylschwingung bei 1675/cm entspricht der des Anthrachinons.



XLIX



L

Eine Methylgruppe in 2-Position des α-Naphthochinons verhindert die Folgereaktionen. Hier wurde das Pyrazolin-diketon L gefasst. Die Additionsrichtung wurde nur aufgrund der Regeln von S. 14 erschlossen.

F. ALKINE

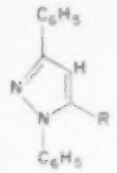
Die Wechselwirkung des Diphenyl-nitrilimins mit der CC-Dreifachbindung führt unmittelbar zum aromatischen Pyrazolsystem. Da schon der Übergangszustand der 1.3-Addition von der beginnenden aromatischen Resonanz profitiert, sollten Alkine besonders aktive Dipolarophile sein. Die wenigen Beispiele der Tabelle 5 vermögen nicht als Bestätigung zu dienen; sie lassen eher sogar gewisse Zweifel an der Überlegenheit der Alkine über die Alkene aufkommen. Erst quantitative Konkurrenzversuche können über die Aktivitätsfolge der Dipolarophilen Aufschluss geben.

Tabelle 5. Additionen des diphenyl-nitrilimins an alkine

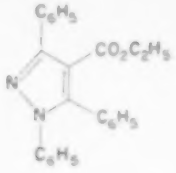
Dipolarophil	Arbeitsweise und Temp.	Addukt		
		Ausb. % d.Th.	Formel	Schmp.
Phenylacetylen	B, 80°	56	LI	138·5–139·5°
Tolan	A, 160°	34	XXXV	215–217°
Tolan	B, 80°	2·6	XXXV	216–218°
Propinal-di-n-propyl-acetal	A, 170°	79	LII	fl.
Propiolsäure-methylester	B, 20°	71	LIV	111·5–112·5°
Phenyl-propiolsäure-äthylester	A, 165°	84	LV	144–145°
Acetylendicarbonsäure-dimethylester	A, 165°	56	LVI	153–154°

Das farblose Addukt des *Phenylacetylens* erwies sich mit dem bekannten 1.3.5-Triphenyl-pyrazol (LI)[20] identisch. Die Orientierung ist also die gleiche wie beim Styrol. Die Umsetzung mit *Tolan* ist weniger ergiebig als die mit Stilben. Das Addukt, das 1.3.4.5-Tetraphenyl-pyrazol, ist identisch mit dem Dehydrierungsprodukt XXXV des Stilben-Addukts (S. 13). Während die Ausbeuten meist nur unwesentlich von der Natur des Diphenyl-nitrilimin-Generators abhängen, scheint im Tolan ein Grenzfall vorzuliegen. Den besseren Erfolg bei der Thermolyse des Diphenyl-tetrazols bringen wir mit der höheren Reaktionstemperatur in Zusammenhang; offensichtlich vermag die 80°-Reaktion (Arbeitsweise B) den Aktivierungsbedarf der 1.3- Dipolaren Addition hier kaum noch zu decken.

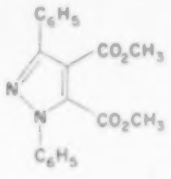
Die unkonjugierte Dreifachbindung des *Propargylaldehyd-acetals* reagierte recht gut. Das ölige Addukt LII lieferte einen kristallinen Aldehyd LIII, dessen Oxydation zur 1.3-Diphenyl-pyrazol-carbonsäure-(5) (XXV) recht energischer Bedingungen



LI R = C_6H_5
LII R = $CH(OC_3H_7)_2$
LIII R = CHO
LIV R = CO_2CH_3



LV



LVI

bedurfte. Die Orientierung ist also die vom sterischen Effekt (S. 14) her vorausgesehene. Auch *Propiolsäureester* befolgte die gleiche Orientierung (Addukt LIV), erwies sich also dem Acrylsäureester analog.

Im Gegensatz zum Zimtester (S. 15) erbrachte *Phenyl-propiolsäureester* ein einheitliches Addukt (LV). Dessen Hydrolyse zur freien Säure und Decarboxylierung oberhalb 200° gab das obenerwähnte 1.3.5-Triphenyl-pyrazol[20] (LI). Damit ist nachgewiesen, dass Propiolester und Phenyl-propiolester die Addition von VII bezüglich der Carbonesterfunktion entgegengesetzt dirigieren. Mit der Verminderung des sterischen Faktors—Phenyl-propiolester ist ein disubstituiertes Acetylen—dominiert jetzt wieder der elektronische Effekt in der Orientierung.

Das Addukt des *Acetylen-dicarbonsäureesters* LVI lässt keine Wahl bezüglich seiner Konstitution; es ging auch aus der Dehydrierung des Fumarester-Addukts hervor. Die freie 1.3-Diphenyl-pyrazol-dicarbonsäure-(4.5) stimmte in ihren Eigenschaften mit Literaturangaben[18] überein und wurde bei 200° zur ebenfalls bekannten 1.3-Diphenyl-pyrazol-carbonsäure-(4) decarboxyliert.

Es ist unschwer ersichtlich, dass dem neuen Syntheseprinzip erhebliche präparative Bedeutung in der Δ^2-Pyrazolin- und Pyrazolreihe zukommt. Die Anlagerung der Nitrilimine an Mehrfachbindungen mit Heteroatom führte in einigen Fällen zu neuen Heterocyclen, wie in einer späteren Veröffentlichung beschrieben wird.

EXPERIMENTELLER TEIL

2.5-*Diphenyl-tetrazol* (VI)[25].

Benz-phenylhydrazid-chlorid (VIII). Das Verfahren von Pechmann und Seeberger[27] wird durch die Verwendung von Äther als Lösungs- und Verdünnungsmittel reproduzierbar und für grössere Ansätze geeignet.

40 g feingepulv. β-Benzoyl-phenylhydrazin (0·19 Mol) und 48 g Phosphorpentachlorid (0·23 Mol) wurden mit 50 cm³ wasserfreiem Äther unter Rückfluss und Feuchtigkeitsabschluss 10 Stdn. gekocht. In die nahezu klare Lösung liessen wir 80 g Phenol in 60 ccm Äther und sodann 80 cm³ Methanol einfliessen. Der grösste Teil des Äthers wurde auf dem Wasserbad abgedampft, bis die Innentemp. der siedenden Lösung 60–70° betrug. Nach Aufbewahren über Nacht im Kühlschrank wurde vom auskristallisierten VIII abgesaugt. Das Umlösen erfolgte aus wenig siedendem Aceton unter Zusatz von Wasser bis zur Trübung. Zweimaliges Umkristallisieren führte zu 25 g gelblichen Prismen (58% d.Th.) mit Schmp. 129·5–130·5° (Lit.[27] 131°).

Gespannte Doppelbindungen

1.3-*Diphenyl*-4.7-*methano*-3a.4.5.6.7.7a-*hexahydro-indazol* (IX). 460 mg VIII (1·99 mMol) und

[25] O. Dimorth und S. Merzbacher, *Ber. Dtsch. Chem. Ges.* **40**, 2402 (1907); vgl. R. Huisgen und M. Seidel, *loc. cit.*[16]

[27] H. v. Pechmann, *Ber. Dtsch. Chem. Ges.* **27**, 320 (1894); H. v. Pechmann und L. Seeberger, *Ibid.* **27**, 2121 (1894).

0·50 g Norbornen (5·3 mMol) wurden in 4 cm³ wasserfreiem Benzol gelöst und bei Raumtemp. mit 1·0 cm³ Triäthylamin (7·15 mMol) versetzt. Nach ca. 10 Sek. setzte die Ausscheidung der farbl. Nadeln des Triäthylammoniumchlorids ein, die nach mehrstdg. Stehen abgesaugt und mit Benzol gewaschen wurden: 272 mg (99% d.Th.) mit Schmp. 253–255° (Lit.[28] 253–254°). Die rote Benzollösung wurde vom Solvens befreit und der Rückstand aus 30 cm³ absol. Äthanol umkristallisiert: 490 mg IX in hellgelben, bei 170·5–171·5° schmelzenden Nadeln (85% d.Th.). Nach 4-maligem Umlösen aus Äthanol lag der Schmp. bei 171–172°.

$C_{20}H_{20}N_2$ (288·4) Ber. C, 83·30; H, 6·99; N, 9·71.
Gef. C, 83·29; H, 7·23; N, 9·57.

Die U.V.-Absorption in Chloroform zeigt Maxima bei 244 mμ (log ε = 4·14) und 370 mμ (log ε = 4·32). Die kräftige blaugrüne Fluoreszenz ist schon bei Tageslicht gut erkennbar. Die braungelbe Lösung in konz. Schwefelsäure wird auf Zusatz von wenig konz. Salpetersäure intensiv dunkelgrün und schlägt schliesslich nach rot um (Knorr-Test[14]).

In einem weiteren Versuch liessen wir das Triäthylamin in die *siedende* Benzollösung von VIII und Norbornen eintropfen. Die Aufarbeitung nach 90 Min. erbrachte 98% d.Th. Triäthylammoniumchlorid und 94% IX.

Umsetzung in wässrigem Alkali. Die Lösung von je 500 mg VIII (2·17 mMol) und Norbornen (5·3 mMol) in 5 cm³ Benzol wurde mit 200 mg KOH (3·5 mMol) in 1·5 cm³ Wasser 8 Stdn. bei Raumtemp. geschüttelt. Die Aufarbeitung der tiefroten Benzolphase ergab 475 mg IX mit Schmp. 170–171·5° (76% d.Th.).

Bromierung. IX reagierte in Chloroform mit 1·0 Moläquival. Brom exotherm. Nach mehreren Stdn. wurde mit Kalilauge und Wasser gewaschen und vom Lösungsmittel befreit. Bei 120–140° (Badtemp.)/0·003 Torr ging ein grüngelbes Sublimat über, das mehrfach aus Äthanol umgelöst wurde: Hellgelbe Blättchen vom Schmp. 133–134°.

$C_{20}H_{19}BrN_2$ (367·3) Ber. C, 65·40; H, 5·21; N, 7·63.
Gef. C, 65·54; H, 5·53; N, 7·48.

Das I.R.-Spektrum entspricht einem 1-[p-*Bromphenyl*]-3-*phenyl*-4.7-*methano*-3a.4.5.6.7.7a-*hexahydro-indazol*. Es unterscheidet sich von dem des Pyrazolins IX im Auftreten zweier neuer Banden bei 800 und 825/cm, den CH-Waggingschwingungen des *p*-disubst. Benzolkerns; die Extinktion der Banden des monosubst. Kerns ist gegenüber IX vermindert.

1.3-*Diphenyl*-4.8-*methano*-3a.4.4a.7a.8.8a-*hexahydro-indeno*-[5.6-*c*]-*pyrazol* (X).

Mit 2.5-*Diphenyl-tetrazol.* 2·0 g VI (9·0 mMol) wurden in 10 cm³ Dicyclopentadien auf 160–165° erhitzt, wobei innerhalb 3 Stdn. 9·0 mMol Stickstoff freigesetzt wurden. Nach dem Abdestillieren des überschüssigen Dipolarophils unter 10 Torr wurde der Rückstand aus Alkohol umkristallisiert zu 2·01 g blassgrüngelben Nadeln mit Schmp. 173–174°. Ausbeute 68% d.Th.

$C_{23}H_{22}N_2$ (326·5) Ber. C, 84·62; H, 6·79; N, 8·58.
Gef. C, 84·43; H, 7·14; N, 8·52.

Mit Benz-phenylhydrazid-chlorid. In die siedende Lösung von 460 mg VIII (1·99 mMol) und 1·2 g Dicyclopentadien (9·1 mMol) in 6 cm³ Benzol liessen wir 1·0 cm³ Triäthylamin einfliessen und kochten 1 Stde. unter Rückfluss. Nach dem Absaugen von 266 mg Triäthylammoniumchlorid (97% d.Th.) wurde eingeengt und aus Äthanol umgelöst. Unter Aufarbeitung der Mutterlauge wurden 568 mg X (87% d.Th.) in hellgelben, grün fluoreszierenden Nadeln isoliert, die nach mehrfachem Umlösen bei 175–176° schmolzen und mit dem aus VI bereiteten Präparat keine Depression gaben. Die Chloroformlösung zeigt Absorptionsmaxima bei 242 mμ (log ε = 4·15) und 370 mμ (log ε = 4·33).

Dehydrierung mit Chloranil. 3·0 g X (9·2 mMol) wurden mit 3·0 g Chloranil (12 mMol) in 20 cm³ Xylol 42 Stdn. rückflussgekocht. Die schwarzbraune Lösung wurde mehrfach mit 4-proz. Kalilauge ausgezogen, mit Wasser gewaschen und im Vak. vom Solvens befreit. Nach Destillation bei 120–165° (Badtemp.)/0·003 Torr wurde die rotbraune glasige Masse aus 60 cm³ heissem Alkohol kristallisiert. Erneutes Umlösen ergab 0·90 g Kristalle, die nach Sublimation im Hochvak. farblos waren. Erst nach 10-maligem Umlösen aus Äthanol verschwand die blaugrüne Fluoreszenz, die von Verunreinigung

[28] L. Wagner, *Z. Krist.* **43**, 148 (1907).

durch X herrührte. Die farbl. Stäbchen des 1.3-*Diphenyl*-4.8-*methano*-4.4a.7a.8-*tetrahydro-indeno*-[5.6-c]-*pyrazols* (XI) schmolzen bei 124–124·5°.

$C_{23}H_{20}N_2$ (324·4) Ber. C, 85·15; H, 6·21; N, 8·64.
Gef. C, 85·03; H, 6·08; N, 8·59.

Reaktion von X *mit Schwefel.* 653 mg X (2·0 mMol) wurden mit 90 mg Schwefel (2·8 mMol) im Mikrokölbchen im Verlauf von 3 Stdn. von 200 auf 255° erhitzt, worauf die H_2S-Entwicklung abgeschlossen war. Die Sublimation bei 120–170° (Badtemp.)/0·01 Torr gab 203 mg nahezu farbl. Kristalle (46% d.Th.) mit Schmp. 80–85°, die durch Tieftemperaturkristallisation aus Petroläther in Nadelbüscheln mit Schmp. 84–85° erhalten wurden. Mischschmp. und I.R.-Spektrum bewiesen die Identität mit 1.3-*Diphenyl-pyrazol* (XII), das zum Vergleich aus Benzoylacetaldehyd und Phenylhydrazin erhalten wurde (Lit.[22] 84°).

1.3-*Diphenyl*-4.7-*methano*-3a.4.7.7a-*tetrahydro-indazol* (XIII). Die Lösung von 1·99 mMol VIII und 2·25 g Bicycloheptadien (24·7 mMol) in 7 cm³ Benzol wurde mit 1·0 cm³ Triäthylamin 3 Stdn. auf 65° erhitzt und über Nacht bei Raumtemp. aufbewahrt. Die orangefarbene Lösung wurde von 1·97 mMol Triäthylammonium-chlorid abgesaugt und eingedampft. In 50 cm³ siedendem Alkohol blieben 27 mg XIV ungelöst. Die Lösung lieferte 451 mg blassgrüngelbe Kristalle (79% XIII), die sich nach Sintern gegen 122° bei 133–135° unter Gasentwicklung zersetzten. Ein aus Petroläther (80–120°) umgelöstes und bei 20° im Hochvak. getrocknetes Präparat wurde analysiert. U.V.-Absorptionsbanden in Chloroform: 243 mμ (log ε = 4·13) und 369 mμ (log ε = 4·30).

$C_{20}H_{18}N_2$ (286·4) Ber. C, 83·88; H, 6·33; N, 9·78.
Gef. C, 83·76; H, 6·40; N, 9·88.

Bei dem alkoholunlöslichen Anteil handelt es sich um 6% d.Th. an 1.3.5.7-*Tetraphenyl*-4.8-*methano*-3a.4.4a.7a.8.8a-*hexahydro-pyrazolo*-[4.5-f]-*indazol* (XIV). Zusammen mit dem Produkt eines weiteren Ansatzes wurde es mehrfach aus Dimethylformamid umgelöst zu einem hellgrüngelben Pulver, das oberhalb 260° dunkel wird und oberhalb 320° unter Zers. schmilzt. U.V.-Absorptionsmaxima in Chloroform: 244 mμ (log ε = 4·39) und 359 mμ (log ε = 4·52).

$C_{33}H_{28}N_4$ (480·6) Ber. C, 82·47; H, 5·87; N, 11·66.
Gef. C, 82·48; H, 6·23; N, 11·90.

Thermolyse von XIII. 2·29 g XIII (8·0 mMol) wurden in einem Mikrokölbchen mit 2 hintereinander geschalteten Vorlagen, die zweite mit Trockeneis gekühlt, langsam von 130° auf 185° erhitzt. Die Zersetzung unter kräftiger Gasentwicklung war nach wenigen Min. abgeschlossen. In der Kühlvorlage hatten sich 406 mg *Cyclopentadien* (77% d.Th.) gesammelt; die Identifizierung erfolgte über das bei 165–166·5° schmelzende Maleinsäureanhydrid-Addukt. Aus dem Rückstand gingen bei 135–150° (Badtemp.)/0·003 Torr 1·73 g (98% d.Th.) über, die zu farbl. Kristallkrusten erstarrten. Der Schmp. 84·5–86° erfuhr in der Mischung mit authent. 1.3-*Diphenyl-pyrazol* (XII) keine Erniedrigung.

1.3-*Diphenyl*-4.7-*methano*-3a.4.5.6.7.7a-*hexahydro-indazol-dicarbonsäure*-(5.6)-*anhydrid* (XV). In die rückflusssiedende Lösung von 2·00 mMol VIII und 4·00 mMol *endo-cis*-Bicyclo-[2.2.1]-hepten-(5)-dicarbonsäure-(2.3)-anhydrid[20] in 4 cm³ Benzol wurden innerhalb 1 Stde. 1·0 cm³ Triäthylamin und 2 cm³ Benzol eingetropft. Nach weiterem 1-stdg. Kochen liessen wir erkalten und saugten ab. Aus 665 mg Niederschlag liessen sich mit Wasser 274 mg Triäthylammoniumchlorid (2·00 mMol) auswaschen. 391 mg Rückstand wurden aus Essigester zu blassgrüngelben Tafeln mit Schmp. 279–281° u. Zers. umgelöst (55% d.Th.).

$C_{22}H_{18}N_2O_3$ (358·4) Ber. C, 73·73; H, 5·06; N, 7·82.
Gef. C, 73·81; H, 5·13; N, 7·78.

Nichtkonjugierte Olefine und Ketone

1.3-*Diphenyl*-5-n-*pentyl*-Δ^2-*pyrazolin* (XVI). 3·98 mMol VIII wurden mit 21·5 mMol Hepten-(1) unter Zusatz von 1·5 cm³ Triäthylamin im Einschmelzrohr 30 Stdn. auf 80–90° erhitzt. Die vom

[22] L. Knorr und P. Duden, *Ber. Dtsch. Chem. Ges.* **26**, 111 (1893).
[20] O. Diels und K. Alder, *Liebigs Ann.* **460**, 98 (1928).

Triäthylammoniumchlorid (100%) abgesaugte Lösung wurde eingedampft und destilliert. Das bei 160–180° (Badtemp.)/0·001 Torr übergetriebene gelbe Öl kristallisierte aus Methanol zu 1·00 g gelben Nadeln (85%) mit Schmp. 54–57°. Zweimaliges Umlösen aus Methanol steigerte den Schmp. auf 56–58°.

$C_{20}H_{24}N_2$ (292·4) Ber. C, 82·15; H, 8·27; N, 9·58.
Gef. C, 82·17; H, 8·30; N, 9·68.

Ein weiterer Ansatz mit 3·5 Moläquival. Hepten-(1) in siedendem Benzol ergab 93% gelbes Rohdestillat an XVI.

Oxydation zu XXV. 0·22 g XVI (0·75 mMol) wurden mit 1·5 mMol Chloranil in 25 cm³ Xylol durch 2 stdg. Rückflusskochen dehydriert. Die übliche Aufarbeitung führte zu einem blassgelben öligen Destillat. Das rohe 1.3-*Diphenyl*-5-n-*pentyl-pyrazol* wurde in siedendem 50-proz. Pyridin mit 2 g Kaliumpermanganat 80 Min. oxydiert. Nach Ausäthern wurde vom Braunstein filtriert und unter Zusatz von Sulfit angesäuert. Die sich ausscheidende Carbonsäure (0·13 g) schmolz nach Umlösen aus Methanol-Wasser bei 225–226° und stimmte im I.R.-Spektrum mit 1.3-*Diphenyl-pyrazol-carbonsäure*-(5) (XXV) überein.

9-[1.3-*Diphenyl*-Δ^2-*pyrazolinyl*-(5)]-*nonansäure-äthylester* (XVII). 3·98 mMol VIII wurden mit 16·5 mMol Undecylensäure-äthylester (techn.), wie für XVI beschrieben, umgesetzt. Bei 200–230° (Badtemp.)/0·003 Torr gingen 1·30 g Rohprodukt (80% d.Th.) über. Aus Methanol gelbe Nadeln mit Schmp. 40–42°.

$C_{26}H_{34}N_2O_2$ (406·6) Ber. C, 76·81; H, 8·43; N, 6·89.
Gef. C, 76·55; H, 8·49; N, 7·12.

Beim Versuch mit 3 Moläquival. des ungesätt. Esters in siedendem Benzol liessen sich aus dem Destillat durch Kristallisation 220 mg *Tetraphenyl-dihydrotetrazin* XVIII (28% d.Th.) mit Schmp. 200–203° abtrennen (Lit.[31] 204°); Identifizierung mittels I.R.-Spektrum.

1.3-*Diphenyl*-cis-1.3a.4.5.6.6a-*hexahydro-cyclopentapyrazol* (XIX). Die Umsetzung von 1·99 mMol VIII, 0·77 g Cyclopenten (11·3 mMol) und Triäthylamin in 5 cm³ Benzol wurde durch 150 Min. Rückflusskochen und Aufbewahren über Nacht bei Raumtemp. durchgeführt. Nach Abfiltrieren von 95% d.Th. Triäthylammoniumsalz wurde im Hochvak. sublimiert und aus Alkohol umgelöst: 408 mg blassgelber, blaugrün fluoreszierender Nadeln (78% d.Th.) mit Schmp. 137·5–139°. Maxima der U.V.-Absorption in Chloroform: 241 mμ (log ε = 4·12) und 365 mμ (log ε = 4·31).

$C_{18}H_{18}N_2$ (262·4) Ber. C, 82·41; H, 6·91; N, 10·68.
Gef. C, 81·94; H, 6·88; N, 10·47.

1.3.4.4-*Tetraphenyl*-Δ^2-*pyrazolon*-(5) (XX?). Unter Stickstoff wurden 2·00 mMol VIII mit 0·7 g Diphenylketen (3·5 mMol) und Triäthylamin in siedendem Benzol umgesetzt. Nach Absaugen von 89% d.Th. Triäthylammoniumchlorid und Entfernen des Lösungsmittels wurden bei 150–220° (Badtemp.)/0·001 Torr 1·06 g rotes Öl übergetrieben. Aus Alkohol kristallisierten 0·19 g orangefarbene Nadeln mit Schmp. 160–162°; die Amid-I-Bande liegt bei 1712/cm. Weitere kristalline Fraktionen aus der Mutterlauge bedürfen noch der Untersuchung.

$C_{27}H_{20}N_2O$ (388·5) Ber. C, 83·48; H, 5·19; N, 7·21.
Gef. C, 83·22; H, 5·09; N, 7·29.

1.3-*Diphenyl*-5-*äthoxy-pyrazol* (XXI). Die Reaktion von 2·00 mMol VIII und 0·88 g Ketendiäthylacetal (7·6 mMol) mit Triäthylamin in siedendem Benzol ging ohne Abscheidung des Triäthylammoniumsalzes vonstatten. Bei 160–170° (Badtemp.)/0·004 Torr gingen 0·50 g eines roten Öls über, das in Benzollösung an Aluminiumoxyd (Merck, Akt. I) chromatographiert wurde. Aus den ersten Eluaten wurden durch Umlösen aus 90-proz. Alkohol 0·42 g farbl. Nadeln vom Schmp. 67–69° erhalten. Das U.V.-Absorptionsmaximum (Chloroform) bei 275 mμ (log ε = 4·36) entspricht nahezu dem des 1.3-Diphenyl-pyrazols bei 279 mμ (log ε = 4·34).

$C_{17}H_{16}N_2O$ (264·3) Ber. C, 77·24; H, 6·10; N, 10·60.
Gef. C, 76·92; H, 6·24; N, 10·56.

[31] E. Bamberger und J. Grob, *Ber. Dtsch. Chem. Ges.* **34**, 523 (1901).

Hydrolyse zu 1.3-*Diphenyl-Δ²-pyrazolon*-(5) (XXII). 0·53 g XXI wurden in 5 cm³ Äthanol und 7 cm³ konz. Salzsäure 9 Tage rückflussgekocht, wobei sich ein hellbrauner Niederschlag abschied. Nach Neutralisation mit NaOH wurde mit Methylenchlorid aufgenommen und dessen Rückstand im Hochvak. destilliert. Durch Umlösen aus Äthanol und Leichtbenzin (80–110°) wurden geringe Mengen XXI entfernt: 0·35 g farbl. XXII (75% d.Th.) mit Schmp. 136–137·5°, die sich im Mischschmp. identisch erwiesen mit einem Präparat, das aus Benzoylessigsäure-äthylester und Phenylhydrazin (Lit.[17] 137°) bereitet wurde. Auch die I.R.-Spektren mit der starken Carbonylschwingung bei 1708/cm stimmten überein.

Konjugierte Alkene

1.3-*Diphenyl-5-vinyl-Δ²-pyrazolin* (XXIII). 2·31 g VIII (10·0 mMol) und 2·5 l Butadien, in 40 cm³ Benzol gelöst, wurden mit 3 cm³ Triäthylamin unter Butadiendruck bei Raumtemp. 4 Stdn. geschüttelt. Nach mehrtäg. Aufbewahren wurde die blaufluoreszierende Lösung von 9·8 mMol Triäthylammoniumchlorid abgesaugt. Der Rückstand der Benzollösung wurde aus Äthanol umkristallisiert zu 2·34 g XXIII in blassgelben, bei 76–77·5° schmelzenden Nadeln. Sdp. 130–140° (Badtemp.)/0·001 Torr.

$C_{17}H_{16}N_2$ (248·3) Ber. C, 82·22; H, 6·50; N, 11·28.
Gef. C, 82·58; H, 6·59; N, 11·34.

Dehydrierung zu XXIV. 4·0 mMol XXIII wurden mit 4·7 mMol Chloranil in 10 cm³ Xylol 10 Stdn. rückflussgekocht. Nach Absaugen von 2·9 mMol Tetrachlorhydrochinon wurde mit Alkali ausgezogen, gewaschen und eingeengt. Bei 155–180° (Badtemp.)/0·001 Torr gingen 0·87 g Rohprodukt (89% d.Th.) als rotes viskoses Öl über, dessen Kristallisation nicht gelang.

Oxydation von XXIV. 0·61 g rohes XXIV wurden in 45 cm³ stabilem Aceton unter Rühren innerhalb von 2 Stdn. mit 1·25 g Kaliumpermanganat versetzt. Nach weiteren 30 Min. wurde mit schwefliger Säure reduziert und mit Methylenchlorid ausgezogen. Den Rückstand der organischen Phase kristallisierten wir aus Tetrachlorkohlenstoff und wenig Methanol um zu 0·41 g farbl. Nadeln (63%) mit Zersp. 227–228·5°. Weiteres Umlösen steigert den Schmp. u. Zers. auf 229–231°, ohne Depression mit authent. 1.3-*Diphenyl-pyrazol-carbonsäure*-(5) (XXV). Auch die I.R.-Spektren sind identisch.

Unabhängige Synthese der 1.3-*Diphenyl-pyrazol-carbonsäure*-(5) (XXV). Der aus Benzal-acetessigester und Phenylhydrazin bereitete 1.3-*Diphenyl-5-methyl-pyrazolin-carbonsäure*-(4)-*äthylester*[18] wurde mit Chloranil in Xylol zum Pyrazol XLII dehydriert. Alkalische Verseifung und Decarboxylierung ergaben das 1.3-*Diphenyl-5-methyl-pyrazol*,[18] das nach Umlösen aus Äther-Petroläther bei 45–47° schmolz (Lit.[22] 47°). 2·0 g davon (8·5 mMol) wurden mit 6 g Kaliumpermanganat in 50 cm³ stabilem Pyridin und 50 cm³ Wasser 2 Stdn. unter Rückfluss gekocht. Nach dem Filtrieren wurde mit 2 n HCl eben angesäuert. Das nach dem Erkalten ausgeschiedene Produkt wurde durch Umlösen aus Methanol in 31% Ausgangsmaterial und 24% d.Th. XXV mit Schmp. 228–229° u. Zers. getrennt; die Titration mit n/10 NaOH gegen Phenolphthalein ergab das Säureäquivalent 261.

$C_{16}H_{12}N_2O_2$ (264·3) Ber. C, 72·71; H, 4·58; N, 10·60.
Gef. C, 72·60; H, 4·96; N, 10·79.

1.3-*Diphenyl*-cis-1.3a.4.6a-*tetrahydro-cyclopentapyrazol* (XXVI). 1·99 mMol VIII wurden mit 0·20 g Cyclopentadien (3·0 mMol) und Triäthylamin bei Raumtemp. umgesetzt. Nach 20 Stdn. hatte sich XXVI teilweise schon ausgeschieden; der Rest wurde aus der Benzollsg. gewonnen. Nach Umlösen aus Alkohol und Hochvakuumsublimation wurden 0·30 g blassgelbe Blättchen mit Schmp. 183–184° erhalten. Maxima der U.V.-Absorption in Chloroform: 242 mμ (log ε = 4·11) und 367 mμ (log ε = 4·31).

$C_{18}H_{16}N_2$ (260·3) Ber. C, 83·04; H, 6·20; N, 10·76.
Gef. C, 83·15; H, 6·43; N, 10·70.

Die *Oxydation* mit Kaliumpermanganat in Aceton bei Raumtemp. lieferte wenig 1.3-Diphenyl-pyrazol-carbonsäure-(4) neben Benzoesäure. Die Behandlung von XXVI mit 1·0 Moläquival. Brom

[22] K. v. Auwers und K. Schaum, *Ber. Dtsch. Chem. Ges.* **62**, 1671 (1929).

in Benzol führte unter HBr-Entwicklung zum 1-[4-*Bromphenyl*]-3-*phenyl*-cis-1.3a.4.6a-*tetrahydro-cyclopentapyrazol*, das im I.R.-Spektrum die *p*-Disubstitutionsbande bei 820/cm aufweist. Aus Äthanol blassgrüngelbe Blättchen mit Schmp. 148–150°.

$C_{18}H_{15}BrN_2$ (339·2) Ber. N, 8·26. Gef. N, 8·55.

Katalytische Hydrierung von XXVI. 300 mg in 80 cm³ Essigester nahmen bei 20° in Gegenwart von Raney-Nickel innerhalb 50 Min 1·1 Moläquival. Wasserstoff auf. Aus Äthanol kamen unter Aufarbeitung der Mutterlauge 0·29 g mit Schmp. 137–139°, mit XIX identisch in Mischschmp. und I.R.-Spektrum.

1.3-*Diphenyl*-3a.4.5.7a-*tetrahydro-indazol* (XXVII). Das nach Arbeitsweise B mit 5 Moläquival. Cyclohexa-1.3-dien in 73% Ausbeute erhaltene Addukt ging bei 150–160° (Badtemp.)/0·005 Torr über und kristallisierte aus Äthanol in hellgrüngelben Nadeln mit Schmp. 119·5–121°.

$C_{19}H_{18}N_2$ (274·4) Ber. C, 83·18; H, 6·61; N, 10·21.
Gef. C, 83·37; H, 6·75; N, 10·28.

1.3-*Diphenyl-indazol* (XXVIII). 2·00 mMol XXVII wurden mit 4·88 mMol Chloranil in 10 cm³ Xylol 18 Stdn. gekocht und wie üblich aufgearbeitet. Nach Hochvak. destillation kamen aus Methanol 426 mg farblose Spiesse (79% d.Th.) mit Schmp. 100·5–102°, die sich in der Mischprobe mit dem nach[19]-dargestellten Produkt (Schmp. 100–101°) identisch erwiesen.

$C_{19}H_{14}N_2$ (270·3) Ber. C, 84·42; H, 5·22; N, 10·36.
Gef. C, 84·28; H, 5·53; N, 10·54.

1.3.5-*Triphenyl*-Δ^2-*pyrazolin* (XXIX). 1·99 mMol VIII wurden mit 0·91 g frisch destilliertem Styrol (8·7 mMol) und Triäthylamin in Gegenwart von etwas Hydrochinon in Benzol 2 Stdn. bei 60° umgesetzt. Die übliche Aufarbeitung erbrachte 523 mg XXIX (88% d.Th.) in grüngelben Nadeln, die nach Umlösen aus Methanol bei 137–138° schmolzen. Die Verbindung stimmte mit einem authent. Präparat von XXIX (Lit.[20] 134–135°) in Mischschmp. und I.R.-Spektrum überein. Das U.V.-Spektrum in Chloroform besitzt Maxima bei 240 mμ ($\log \varepsilon = 4{\cdot}20$) und 361 m$\mu$ ($\log \varepsilon = 4{\cdot}28$).

1.3-*Diphenyl*-3a.4.5.9b-*tetrahydro-naphtho*-[1.2-c]-*pyrazol* (XXX)

Mit 2.5-*Diphenyl-tetrazol*. 2·0 g VI (9·0 mMol) spalteten beim 3-stdg. Erhitzen in 5 cm³ 1.2-Dihydronaphthalin auf 155–165° 0·98 Moläquival. Stickstoff ab. Nach Abziehen des Dihydronaphthalins i.Vak. kamen aus Methanol 2·44 g gelbgrüne Nadeln (84%) mit Schmp. 138–148°. Eine häufig umgelöste Probe, die immer noch den breiten Schmelzbereich von 143–149° aufwies, gab korrekte Analysenwerte.

$C_{23}H_{20}N_2$ (324·4) Ber. C, 85·15; H, 6·21; N, 8·64.
Gef. C, 85·13; H, 6·36; N, 8·82.

Mit Benz-phenylhydrazid-chlorid. Nach Arbeitsweise B wurden mit 3·5 Moläquival. 1.2-Dihydronaphthalin 75% d.Th. hellgrüngelbe Nadeln vom Schmp. 148–150° erhalten. Nach 4-maligem Umkristallisieren aus Äthanol lag der Schmp. bei 151–152°. Die I.R.-Spektren der beiden Präparate stimmen weitgehend überein.

$C_{23}H_{20}N_2$ (324·4) Ber. C, 85·15; H, 6·21; N, 8·64.
Gef. C, 84·96; H, 6·46; N, 8·67.

Dehydrierung zu 1.3-*Diphenyl-naphtho*-[1.2-c]-*pyrazol* (XXXI). Chloranil in siedendem Xylol ergab ein Gemisch mit Ausgangsmaterial. 1·0 mMol XXX und 2·5 mMol Chloranil wurden in 5 cm³ Trichlorbenzol 52 Stdn. auf 170° erhitzt. Das wie üblich aufgearbeitete Produkt kristallisierte nach Hochvak. destillation beim Anreiben mit Petroläther: 70% d.Th. XXXI in farbl. Nadeln, die nach mehrfachem Umlösen aus Petroläther und aus Äthanol bei 100·5–102° schmolzen.

$C_{23}H_{16}N_2$ (320·4) Ber. C, 86·22; H, 5·03; N, 8·75.
Gef. C, 86·23; H, 5·34; N, 8·84.

VOL. 17 1962

Synthese des 1.3-*Diphenyl-naphtho*-[1.2-c]-*pyrazols* (XXXI). 2·48 g 2-*Benzoyl-naphthol*-(1)[33] (10 mMol) wurden mit 1·2 cm³ Phenylhydrazin und 20 mg *p*-Toluolsulfonsäure in 5 cm³ Äthylglykol 16 Stdn. unter N_2 auf 150° erhitzt. Nach Einrühren in Wasser kristallisierte das rotbraune Produkt langsam durch. Umlösen aus Äthanol gab 2·44 g (72% d.Th.) *Phenyl*-[1-*hydroxy-naphthyl*-(2)]-*keton-phenylhydrazon* (XXXII) in derben orangegelben Prismen; Schmp. 130–131·5°. Siedet unzersetzt bei 220–230°/0·001 Torr.

$C_{23}H_{18}N_2O$ (338·4) Ber. C, 81·63; H, 5·36; N, 8·28.
Gef. C, 81·72; H, 5·43; N, 8·47.

1·02 g XXXII (3·0 mMol) lösten sich innerhalb 2 Stdn. in 70 cm³ Polyphosphorsäure bei 95°. Nach Eingiessen in 200 cm³ Eiswasser schieden sich bei 4-täg. Aufbewahren gelbe Flocken ab, die bei 210–230° (Badtemp.)/0·001 Torr übergetrieben wurden. Das orangegelbe Destillat wurde aus Benzol an Aluminiumoxyd (Woelm, sauer, Akt. I) chromatographiert. Aus Petroläther 0·56 g XXXI in farbl. Nadeln mit Schmp. 102–103°. Mischschmp. und I.R.-Spektrum bewiesen die Identität mit dem aus XXX erhaltenen Produkt.

1.3-*Diphenyl*-3a.8b-*dihydro*-4H-*indeno*-[1.2-c]-*pyrazol* (XXX, CH_2 statt CH_2—CH_2). Die Umsetzung mit 3·5 Moläquival. Inden nach Methode B lieferte 100% Triäthylammoniumchlorid sowie nach Sublimation bei 140–170° (Badtemp)/0·004 Torr und Umlösen aus Äthanol/Methylenchlorid 482 mg hellgelbe Nadeln mit Schmp. 171–172°. Die Chloroformlösung zeigt folgende Maxima der U.V.-Absorption: 239 mμ (log ε = 4·15) und 364 mμ (log ε = 4·28).

$C_{22}H_{18}N_2$ (310·4) Ber. C, 85·13; H, 5·84; N, 9·03.
Gef. C, 85·53; H, 5·88; N, 9·12.

1.3.4.5-*Tetraphenyl*-4.5-trans-*dihydro-pyrazol* (XXXIII). Die Arbeitsweise B mit 2·8 Moläquival. *trans*-Stilben in Benzol führte zu 86% d.Th. blassgrüngelben, verfilzten Nadeln mit Schmp. 166·5–168° (Äthanol).[34]

$C_{27}H_{22}N_2$ (374·5) Ber. C, 86·60; H, 5·92; N, 7·48.
Gef. C, 86·14; H, 5·61; N, 7·47.

Die *Dehydrierung zu* 1.3.4.5-*Tetraphenyl-pyrazol* (XXXV) gelang mit Chloranil beim 50-stdg. Kochen in Xylol. Hochvak. destillation und Umlösen aus Cyclohexan führten zu 88% farbl. Kristallen mit Schmp. 217–219°. Die Übereinstimmung mit dem Addukt des Tolans (S. 28) ist beweisend für die Konstitution.[35]

1.3.4.5-*Tetraphenyl*-4.5-cis-*dihydro-pyrazol* (XXXIV). 4·0 mMol VIII wurden mit 3·6 g *cis*-Stilben (20 mMol) 3 Tage im Einschmelzrohr auf 50° erhitzt. Das wie üblich isolierte Addukt (0·79 g, 53% d.Th.) kristallisierte aus Methylenchlorid/Äthanol in grünlichgelben Nadeln vom Schmp. 194·5–195·5°.

$C_{27}H_{22}N_2$ (374·5) Ber. C, 86·60; H, 5·92; N, 7·48.
Gef. C, 86·23; H, 5·79; N, 7·56.

Zur *Dehydrierung* wurden 110 mg XXXIV in 5 cm³ siedendem, stabilem Aceton nach und nach mit 60 mg $KMnO_4$ in 20 cm³ Aceton versetzt. Nach Behandlung mit schwefliger Säure wurde das Aceton vertrieben: 108 mg 1.3.4.5-*Tetraphenyl-pyrazol* mit Schmp. 217–220°; aus Alkohol farbl. Blättchen. Die Identität mit dem Produkt aus XXXIII und mit Tolan-Addukt (S. 28) wurde durch Mischschmp. und I.R.-Spektrum bestätigt.

7.9-*Diphenyl*-6b.9a-*dihydro-acenaphtho*-[1.2-c]-*pyrazol* (XXXVI). 2·0 mMol VIII wurden mit 6·0 mMol Acenaphthylen nach Methode B 1 Stde. bei 80° und 7 Stdn. bei 20° zur Reaktion gebracht.

° Dieser Versuch wurde von Dr. J. Sauer und I. Ziegler ausgeführt.

[33] S. R. Edminson und T. P. Hilditch, *J. Chem. Soc.* **97**, 223 (1910).

[34] F. Klingemann, *Liebigs Ann.* **269**, 104 (1892), erhielt aus Dibenzoylstilben mit Phenylhydrazin neben weiteren Produkten gelblichbraune Täfelchen mit Schmp. 212–213°. Aufgrund der Analysendaten diskutierte er 1.3.4.5-Tetraphenyl-Δ^2-pyrazolin und 1.3.4.5-Tetraphenyl-pyrazol, um sich dann für das erstere zu entscheiden. Die Eigenschaften stimmen weder mit unserer *cis*- noch mit *trans*-Form überein.

[35] J. Marshall, *J. Chem. Soc.* **107**, 509 (1915), glaubte das 1.3.4.5-Tetraphenyl-pyrazol, Nadeln mit dem Schmp. 167°, aus α.α-Dibenzoyl-toluol mit Phenylhydrazin erhalten zu haben. Er gibt jedoch keine Analysendaten an. Überdies konnten A. Garcia-Banús und L. Medrano, *An. Soc. Espanola Fis. Quim.* **21**, 436 (1923); *Chem. Zentr.* **95 I**, 908 (1924), die Reaktion nicht wiederholen.

598 mg Addukt hatten sich bereits mit dem Triäthylammoniumchlorid abgeschieden; die Benzollösung lieferte weitere 26 mg (zus. 90% d.Th.). Aus Toluol kamen blassgelbe Nadeln mit Schmp. 255·5–257·5° u. Zers.

$C_{25}H_{18}N_2$ (346·4) Ber. C, 86·67; H, 5·24; N, 8·09.
Gef. C, 86·66; H, 5·32; N, 8·28.

1.3-*Diphenyl-dibenzo*-[b.f.]-*pyrazolo*-[3.4-d]-*azepin* (XXXVII).* 1·20 g Dibenzo-[b.f.]-azepin[21] (6·2 mMol) wurden mit 6·2 mMol VIII und 4·3 cm³ Triäthylamin in 10 cm³ Benzol 2½ Stdn. rückflussgekocht. Das schwerlösliche Addukt wurde abgesaugt und durch Waschen mit Wasser vom Triäthylammoniumchlorid befreit: 1·31 g mit Schmp. 248–253° (55% d.Th.). Mehrfaches Umlösen aus Xylol steigerte den Schmp. der gelbgrünen, lebhaft fluoreszierenden Blättchen auf 264–265·5°.

$C_{27}H_{21}N_3$ (387.5) Ber. C, 83.69; H, 5·46; N, 10·85.
Gef. C, 83·71; H, 5·74; N, 11·32.

Die U.V.-Absorption von XXXVII mit Maxima bei 302 mμ (log ε = 4·07) und bei 361 mμ (log ε = 4.14) lässt sich additiv aus der des Imino-dibenzyls und der des Pyrazolinanteils zusammensetzen. Das I.R.-Presslingsspektrum zeigt die NH-Bande bei 3335/cm.

α,β-Ungesättigte Carbonester und Nitrile sowie Chinone

1.3-*Diphenyl-Δ²-pyrazolin-carbonsäure*-(5)-*äthylester* (XXXVIII). Die Arbeitsweise B mit 3 Moläquival. Acrylsäure-äthylester lieferte in 45 Min bei 20° 85% d.Th. grünlichgelbe Nadeln mit Schmp. 99–101° (Methanol). Es ergab sich kein Anhaltspunkt für das Vorhandensein eines zweiten Isomeren.

$C_{18}H_{18}N_2O_2$ (294.3) Ber. N, 9·52. Gef. N, 9·35.

Die *Dehydrierung* mit Chloranil in siedendem Xylol erbrachte 94% d. Th. 1.3-*Diphenyl-pyrazol-carbonsäure*-(5)-*äthylester* in farbl. Nadeln mit Schmp. 84·5–86°. Die Hydrolyse mit methanolischer Kalilauge lieferte 88% d.Th. der Carbonsäure XXV mit Schmp. 222–225° (Zers.). Die Identifizierung mit dem Präparat von S. 22 erfolgte durch Mischschmp. und I.R.-Spektrum.

1.3-*Diphenyl*-5-*cyano*-*Δ²-pyrazolin* (XXXIX). Die Reaktion mit 7 Moläquival. Acrylnitril nach Arbeitsweise B ist bereits nach 30 Min. bei Raumtemp. abgeschlossen. Die Geschwindigkeit der Abscheidung des Triäthylammoniumchlorids hängt offensichtlich von der Natur des Dipolarophilen ab; der Blindversuch ohne Dipolarophil zeigt das augenfällig. Dieses Phänomen wurde bei der Formulierung auf S. 5 nicht beachtet. Die weitere Bearbeitung muss lehren, ob eine Zwischenstufe reversibel gebildet wird oder ob Komplexbildung irgendwelcher Art eine Rolle spielt. Das zu 85% d.Th. anfallende Addukt schmilzt nach Umlösen aus Methanol bei 138–140°.

$C_{16}H_{13}N_3$ (247.3) Ber. C, 77·70; H, 5·30; N, 17·00.
Gef. C, 77·48; H, 5·59; N, 16·88.

Dass das I.R.-Spektrum keine Nitrilbande aufweist, widerspricht nicht der Formel XXXIX, da zahlreiche Präzedenzfälle ausbleibender Nitrilbanden existieren. Mit Chloranil wird das Addukt beim 2-stdg. Kochen in Xylol aromatisiert; die zu 76% erhaltenen farbl. Nadeln des 1.3-*Diphenyl*-5-*cyano-pyrazols* mit Schmp. 133–135° besitzen bei 2240/cm eine deutliche Nitrilbande. Die Hydrolyse des Nitrils wurde durch 2-stdg. Rückflusskochen mit der Mischung gleicher Volumina Schwefelsäure, Eisessig und Wasser vorgenommen, wobei 80% d.Th. 1.3-*Diphenyl-pyrazol-carbonsäure*-(5) mit Schmp. 225–227° u. Zers. resultieren.

1.3.5-*Triphenyl-Δ²-pyrazolin-carbonsäure*-(4)-*äthylester* (XLI). 2·0 g Diphenyl-tetrazol (9·0 mMol) setzten beim Zerfall in 7 cm³ Zimtsäure-äthylester bei 155–165° in 8 Stdn. 97% des berechn. Stickstoffvolumens frei. Nach Entfernung des überschüssigen Zimtesters wurde aus Alkohol zu 2·86 g hellgelben, körnigen Kristallen mit Schmp. 113–116° umgelöst (86% d.Th.). Da die Schmelzgrenzen auch nach wiederholtem Umlösen nicht enger wurden, vermuten wir XLI im Gemisch mit einem zweiten Isomeren. 2·0 g des Gemischs (5·4 mMol) wurden mit 5·7 mMol Chloranil in 10 cm³ Xylol 20 Stdn. rückflussgekocht; die übliche Aufarbeitung ergab farbl. Nadeln mit dem weiten Schmelzbereich 127–133°. Zweimaliges Umlösen aus Alkohol gab zu 50% eine Spitzenfraktion mit Schmp. 142–145°. Der Mischschmp. mit authent. 1.3.5-*Triphenyl-pyrazol-carbonsäure*-(4)-*äthylester* (LV) lag bei 144–145°.

VOL. 17 1962

Die Arbeitsweise B mit 2 Moläquival. Zimtester in siedendem Benzol führte zu 83% d.Th. blassgelber Kristalle, die oberhalb 105° sintern und bei 116–123° schmelzen (Isomerengemisch). Versuche, durch fraktionierte Kristallisation oder chromatographische Adsorption eine Auftrennung zu erzielen, waren noch nicht erfolgreich. Eine häufig aus Äthanol umgelöste Probe, immer noch mit 121·5–124·5 unscharf schmelzend, wurde analysiert.

$C_{28}H_{22}N_2O_4$ (370·5) Ber. C, 77·81; H, 5·99; N, 7·56.
Gef. C, 77·58; H, 6·04; N, 7·50.

1.3-*Diphenyl-5-methyl-pyrazol-carbonsäure-(4)-äthylester* (XLII). 1·0 g VI (4·5 mMol) wurde in 5 cm³ Acetessigsäure-äthylester 2 Stdn. auf 160–170° erhitzt, wobei 104% der berechn. N_2-Menge freigesetzt wurden. Bei 170–180° (Badtemp.)/0·01 Torr gingen 0·92 g eines rasch erstarrenden Öls über (67% d.Th.). Die farbl. Kristalle des Pyrazols XLII schmolzen nach Umlösen aus Cyclohexan/Äther bei 102–104°, ohne Depression mit dem synth. Präparat von S. 22 (Lit.[22] 105°).

$C_{19}H_{18}N_2O_2$ (306·4) Ber. C, 74·49; H, 5·92; N, 9·15.
Gef. C, 74·66; H, 5·70; N, 9·18.

Die gleiche Verbindung, allerdings nur in 19% Ausbeute, wurde bei der Thermolyse von VI in *β*-Äthoxy-crotonsäure-äthylester[36] erhalten; Identifizierung mit Mischschmp. und I.R.-Spektrum. Auch der *β*-Acetoxy-crotonsäure-äthylester[37] lieferte mit zerfallendem VI das Pyrazol XLII, und zwar in 62% Ausbeute.

Die Hydrolyse von XLII mit 12-proz. methanolischer KOH führte zur 1.3-*Diphenyl-5-methyl-pyrazol-carbonsäure*-(4), die nach Umlösen aus Alkohol bei 193–194° u. Zers. schmolz (Lit.[22] 193–194°).

1.3-*Diphenyl-Δ²-pyrazolin*-cis-4.5-*dicarbonsäure-anhydrid* (XLIII). Beim 5-stdg. Erhitzen von 9·0 mMol VI und 6 g Maleinsäureanhydrid in 20 cm³ Anisol auf 155° wurden 115 Mol% Gas entwickelt. Nach Abziehen des Solvens führte das Umlösen aus Benzol zu 1·21 g des grüngelben Addukts XLIII. Der Schmp. 190–192° u.Zers. wurde nur erreicht, wenn man das Röhrchen unmittelbar in ein 180°-Bad brachte.

$C_{17}H_{12}N_2O_4$ (292·3) Ber. C, 69·85; H, 4·14; N, 9·58.
Gef. C, 70·11; H, 4·20; N, 9·53.

Überlässt man VI dem Zerfall in Maleinanhydrid als Solvens bei 160–170°, dann zeigt die hohe Gasentwicklung die Zersetzung von XLIII an. Als nach 3 Stdn. bereits 1·5 Moläquiv. Gas freigesetzt waren, wurde abgebrochen und durch Destillation aufgearbeitet. Bei 180–200° (Badtemp.)/0·001 Torr gingen 35% d.Th. 1.3-*Diphenyl-pyrazol* (XII) über; Schmp. 82–84° (Alkohol).

$C_{15}H_{12}N_2$ (220·3) Ber. C, 81·79; H, 5·49; N, 12·72.
Gef. C, 81·90; H, 5·44; N, 12·48.

1.3-*Diphenyl-Δ²-pyrazolin*-trans-4.5-*dicarbonsäure-dimethylester* (XLIV). Aus 9·0 mMol VI und 5 g Fumarsäure-dimethylester wurden nach Arbeitsweise A unter Entbindung von 0·94 Moläquiv. N_2 2·67 g XLIV (88% d.Th.) in blassgelben Tafeln vom Schmp. 148–150° (Alkohol) erhalten.

$C_{19}H_{18}N_2O_4$ (338·4) Ber. C, 67·45; H, 5·36; N, 8·28.
Gef. C, 67·21; H, 5·32; N, 8·32.

Die Arbeitsweise B mit 2·8 Moläquiv. Fumarester ergab gar 99% d.Th. am Addukt XLIV, das nach Umlösen aus Methanol bei 149·5–151° schmolz und mit obigem Präparat keine Depression zeigte.

Der *trans*-Diester XLIV liess sich auch aus dem *cis*-Anhydrid XLIII bereiten: Beim Aufnehmen in heisser Sodalösung fand offensichtlich schon der Übergang in die *trans*-Reihe statt. Verestern der Dicarbonsäure mit Diazomethan in Äther gab 60% XLIV.

Dehydrierung von XLIV. 1·5 g (4·4 mMol) wurden mit 6·1 mMol Chloranil in Xylol 20 Stdn. rückflussgekocht. Die Kristallisation aus Alkohol ergab 1·17 g farbl. 1.1.3-*Diphenyl-pyrazol-dicarbonsäure*-(4·5)-*dimethylester* mit Schmp. 151–152°, ohne Depression mit dem Addukt LVI des Acetylendicarbonsäureesters.

[36] L. Claisen, *Ber. Dtsch. Chem. Ges.* **26**, 2729 (1893).
[37] L. Claisen und E. Haase, *Ber. Dtsch. Chem. Ges.* **33**, 1242 (1900).

1.3-*Diphenyl*-Δ^2-*pyrazolin*-cis-4.5-*dicarbonsäure-dimethylester* (XLV). Die Arbeitsweise B mit 2·8 Moläquival. Maleinsäure-dimethylester lieferte 93% d.Th. mit Schmp. 149·5–151°, ohne Depression mit dem Fumarester-Addukt XLIV. Ein isomeres Pyrazolin wurde nicht aufgefunden. Neben der basenkatalysierten Stereoisomerisierung XLV → XLIV könnte auch eine Isomerisierung des Maleinsäure- zum Fumarsäureester verantwortlich sein. Möglicherweise enthielt das Triäthylamin bescheidene Mengen des sek. Amins, das bekanntlich die Isomerisierung *cis* → *trans* kräftig katalysiert.[28]

Dagegen gelang es bei der Arbeitsweise A, den *cis*-Diester zu fassen. Im Anschluss an den Zerfall von 9·0 mMol VI in 5 g Maleinsäure-dimethylester wurde der überschüssige Ester abdestilliert. Die fraktionierte Kristallisation des Rückstandes aus Alkohol erlaubte die Trennung von 1·55 g *trans*-Diester XLIV (51% d.Th.) und 0·11 g leichter löslichen, blassgelben Nadeln mit Schmp. 141–143°, die wir als XLV ansprechen (4% d.Th.); kräftige Schmp. depression mit XLIV.

$C_{19}H_{18}N_2O_4$ (338·4) Ber. C, 67·45; H, 5·36; N, 8·28.
Gef. C, 67·81; H, 5·45; N, 8·38.

Als Strukturbeweis kann die Überführung von XLIII in XLV dienen. Nach 3 Tagen Stehen des Anhydrids XLIII in wässrigem Aceton wurden nach Veresterung mit Diazomethan 72% des *cis*-Diesters isoliert, in Schmp., Mischschmp. und I.R.-Spektrum mit XLV identisch.

1.3-*Diphenyl*-4.5-*dimethyl*-Δ^2-*pyrazolin*-cis-4.5-*dicarbonsäure-anhydrid* (XLVI). 9·0 mMol VI und 5·0 g Dimethyl-maleinsäure-anhydrid[51] (39·7 mMol) entwickelten beim 6-stdg. Rückflusskochen in 20 cm³ Anisol 255 cm³ Gas. Nach Abdestillieren des Solvens und des überschüssigen Dipolarophils wurde der Rückstand mit Äther ausgekocht, wobei 1·58 g XLVI (55% d.Th.) ungelöst zurückblieben. Der Schmp. 133–134° stieg auch nach mehrfachem Umlösen der hellgelben derben Polyeder aus Cyclohexan nicht mehr.

$C_{19}H_{16}N_2O_3$ (320·3) Ber. C, 71·24; H, 5·03; N, 8·74.
Gef. C, 71·07; H, 5·01; N, 9·13.

1·3-*Diphenyl*-4.5-*dimethyl*-Δ^2-*pyrazolin*-trans-4.5-*dicarbonsäure-dimethylester* (XLVII). 3·98 mMol VIII wurden mit 2·9 g Dimethyl-fumarsäure-dimethylester[27,43] und 1·5 cm³ Triäthylamin im zugeschmolzenen Rohr 2 Tage auf 50° erwärmt. Die übliche Aufarbeitung ergab nach Umlösen aus Methanol 1·08 g XLVII in gelben Prismen (74% d.Th.); Schmp. 107·5–108·5°.

$C_{21}H_{22}N_2O_4$ (366·4) Ber. C, 68·83; H, 6·05; N, 7·65.
Gef. C, 68·71; H, 6·04; N, 7·72.

1.3-*Diphenyl*-4.5-*dimethyl*-Δ^2-*pyrazolin*-cis-4.5-*dicarbonsäure-dimethylester* (XLVIII). Die Darstellung aus VIII und 5 Moläquival. Dimethyl-maleinsäure-dimethylester[40] folgte der von XLVII. Aus Methanol kristallisierten 0·48 g gelbe Nadeln (33% d.Th.); Schmp. 144–145°.

$C_{21}H_{22}N_2O_4$ (366·4) Ber. C, 68·83; H, 6·05; N, 7·65.
Gef. C, 68·83; H, 6·20; N, 7·72.

Die gleiche Verbindung war auch aus dem *cis*-Anhydrid XLVI zugänglich. Dieses wurde in warmer Kalilauge gelöst, nach dem Erkalten mit Äther überschichtet und unter Eiskühlung mit Salzsäure angesäuert. Die Ätherphase wurde mit Überschuss Diazomethan behandelt. Es resultierten 67% d.Th. des *cis*-Diesters vom Schmp. 144–145°, in I.R.-Spektrum und Mischschmp. mit dem Addukt XLVIII identisch.

1.3-*Diphenyl*-4.9-*dioxo*-4.9-*dihydro-naphtho*-[2.3-c]-*pyrazol* (XLIX). Beim 2-stdg. Erhitzen von 9·0 mMol VI und 3 g α-Naphthochinon (19 mMol) auf 160–170° wurden 96% des berechn. Stickstoffs freigesetzt. Nach Digerieren mit Äther wurde der Rückstand aus Chloroform umkristallisiert: 2·68 g gelbe Nadeln (85% d.Th.) vom Schmp. 257–259°.

$C_{23}H_{14}N_2O_2$ (350·4) Ber. C, 78·84; H, 4·03; N, 7·99.
Gef. C, 78·70; H, 4·10; N, 8·19.

1.3-*Diphenyl*-9a-*methyl*-4.9-*dioxo*-3a.4.9.9a-*tetrahydronaphtho*-[2.3-c]-*pyrazol* (L). 2·25 mMol VI wurden mit 0·6 g 2-Methyl-α-naphthochinon (3·5 mMol) in 5 cm³ Anisol 3 Stdn. rückflussgekocht.

[28] G. R. Clemo und S. B. Graham, *J. Chem. Soc.* 213 (1930).
[29] E. Ott, *Ber. Dtsch. Chem. Ges.* **61**, 2124 (1928).
[40] K. v. Auwers und L. Harres, *Ber. Dtsch. Chem. Ges.* **62**, 1678 (1929).

Aufarbeitung wie bei XLIX gab 0·27 g farbl. Kristalle mit Schmp. 245–247° (Chloroform). Das I.R.-Spektrum zeigt keine OH-Bande; die Carbonylschwingung bei 1780/cm ist auffallend kurzwellig.

$C_{24}H_{18}N_2O_2$ (366·4) Ber. C, 78·66; H, 4·95; N, 7·65.
Gef. C, 78·39; H, 4·75; N, 7·68.

Alkine

1.3.5-*Triphenyl-pyrazol* (LI). 1·30 mMol VIII wurden in 3 cm³ Phenylacetylen auf dem Wasserbad erhitzt und tropfenweise mit 1·0 cm³ Triäthylamin versetzt. Nach 90 Min. liessen wir erkalten, saugten von 95% d.Th. Ammoniumsalz ab und destillierten. Das bei 130–150° (Badtemp.)/0·003 Torr übergehende rote Öl wurde aus Benzol an Aluminiumoxyd (Woelm, basisch, Akt. I) adsorbiert und mit viel Benzol eluiert. Der Rückstand der mittleren Eluate wurde aus Methanol umgelöst zu 0·28 g farbl. LI (72%); Schmp. 138·5–139·5°. Ein aus Dibenzoylmethan und Phenylhydrazin bereitetes Vergleichspräparat (Lit.[29] 137–138°) zeigte in der Mischung keine Depression.

$C_{21}H_{16}N_2$ (296·4) Ber. C, 85·11; H, 5·44; N, 9·45.
Gef. C, 84·77; H, 5·68; N, 9·45.

1.3.4.5-*Tetraphenyl-pyrazol* (XXXV). 9·0 mMol VI setzten beim Erhitzen mit 4 g Tolan (24 mMol) in 6 Stdn. bei 155–165° 235 cm³ N_2 frei. 1·14 g Addukt (34%) kristallisierten aus Alkohol in farbl., bei 215–217° schmelzenden Blättchen. Keine Erniedrigung des Mischschmp. mit dem Dehydrierungsprodukt der Stilben-Addukte.

$C_{27}H_{20}N_2$ (372·4) Ber. N, 7·52. Gef. N, 7·39.

Die Arbeitsweise B mit 2·1 Moläquival. Tolan erwies sich als erheblich unterlegen. Das bei 180–215° (Badtemp.)/0·01 Torr übergehende Öl wurde in Methanol aufgenommen und gab 98 mg des farbl. XXXV mit Schmp. 216–218° (2·6%).

1.3-*Diphenyl-pyrazol-aldehyd*-(5)-*di-n-propylacetal* (LII). Die Arbeitsweise A mit 9·0 mMol VI in 5 cm³ Propargylaldehyd-di-n-propylacetal[41] gab 2·82 g eines bei 190–205° (Badtemp.)/0·001 Torr übergehenden Öls ohne Kristallisationstendenz. Das Addukt LII wurde daher mit einer Mischung aus 20 cm³ Dioxan und 10 cm³ halbkonz. Salzsäure 48 Stdn. bei Raumtemp. hydrolysiert. Zu 79% d.Th. resultierte der 1.3-*Diphenyl-pyrazol-aldehyd*-(5) (LIII), der aus Alkohol in farbl. Nadeln mit Schmp. 138–140° kam.

$C_{16}H_{12}N_2O$ (248·3) Ber. C, 77·40; H, 4·87; N, 11·29.
Gef. C, 77·80; H, 5·16; N, 11·27.

Das rote 2.4-*Dinitrophenylhydrazon* schmilzt gegen 260° u. Zers. Der Aldehyd LIII wurde 2 Stdn. mit nassem Silberoxyd in Methylglykol gekocht. Die Trennung von saurem und neutralem Produkt lieferte 35% 1.3-*Diphenyl-pyrazol-carbonsäure*-(5) mit Schmp. 225–227° u. Zers., ohne Depression mit XXV; daneben wurden 30% LIII zurückisoliert.

1.3-*Diphenyl-pyrazol-carbonsäure*-(5)-*methylester* (LIV). Als Ergebnis der Arbeitsweise B mit 2·5 Moläquival. Propiolsäure-methylester kristallisierten aus Methanol 71% des Addukts LIV in farbl. Nadeln mit Schmp. 109–111°; nach mehrfachem Umlösen stieg der Schmp. auf 111·5–112·5°.

$C_{17}H_{14}N_2O_2$ (278·3) Ber. C, 73·37; H, 5·07; N, 10·06.
Gef. C, 73·13; H, 5·24; N, 10·25.

Die Hydrolyse mit methanolischer KOH gab quantitativ die bei 224–226° u. Zers. schmelzende 1.3-*Diphenyl-pyrazol-carbonsäure*-(5) (XXV).

1.3.5-*Triphenyl-pyrazol-carbonsäure*-(4)-*äthylester* (LV). Der Zerfall von 5·4 mMol VI in 4 g Phenyl-propiolsäure-äthylester führte zu 1·67 g farbl. Nadeln (84% d.Th.) mit Schmp. 144–145° (Äthanol).

$C_{25}H_{20}N_2O_2$ (368·4) Ber. C, 78·24; H, 5·47; N, 7·60.
Gef. C, 77·94; H, 5·48; N, 7·77.

Zur Konstitutionsermittlung wurde LV mit methanolischer KOH verseift zu 90% d.Th. einer farbl. Carbonsäure, die bei 239–241° unter Gasentwicklung schmilzt. Dass es sich um die 1.3.5-*Triphenyl-pyrazol-carbonsäure*-(4) handelt, ging aus der Decarboxylierung bei 245° hervor. Zu 97%

[41] F. Wille und R. Strasser, Dissertation Strasser, Universität München (1959).

d.Th. wurde LI mit Schmp. 137–139° gefasst; der Mischschmp. mit dem Phenylacetylen-Addukt zeigte keine Depression.

1.3-*Diphenyl-pyrazol-dicarbonsäure-(4.5)-dimethylester* (LVI). Das Produkt der Arbeitsweise A mit 9·0 mMol VI und 5 cm³ Acetylen-dicarbonsäure-dimethylester ging bei 210–230° (Badtemp.)/ 0·001 Torr als rasch erstarrendes Öl über. Aus Alkohol schieden sich 1·70 g farbl. Nadeln (56% d.Th.) mit Schmp. 153–154° ab (Lit.[16] 150·5–151·5°).

$C_{19}H_{16}N_2O_4$ (336·3) Ber. C, 67·85; H, 4·80; N, 8·33.
Gef. C, 67·78; H, 4·94; N, 8·23.

Die aus LVI mit KOH in Methanol erhaltene *Dicarbonsäure* schmolz bei 198–200° u. Zers. (Lit.[16] 192–193°) und zeigte ein Säureäquivalent von 170 (Ber. 154). Durch 30 Min. Erhitzen auf 200° wurde sie in die 1.3-*Diphenyl-pyrazol-carbonsäure-(4)* übergeführt, die nach Umlösen aus Alkohol Schmp. 201–203° (Lit.[16] 202–203°) und ein Säureäquivalent von 270 (Ber. 264) aufwies.

Der Deutschen Forschungsgemeinschaft und dem Fonds der Chemischen Industrie danken wir für die wirksame Förderung der Untersuchung. Für die Ausführung der Mikroanalysen sei Herrn H. Schulz und Frau S. Scholz, für die Aufnahme der U.V.-Spektren Frl. I. Ziegler bestens gedankt. Für die freundl. Überlassung von Chemikalien schulden wir den Farbwerken Hoechst (Frankfurt), den Farbenfabriken Bayer (Leverkusen), der BASF (Ludwigshafen), der Du Pont de Nemours (Wilmington, U.S.A.) und der Deutschen Shell A.G. (Hamburg) grossen Dank.

VOL. 17 1962

Tetrahedron, 1962, Vol. 17, pp. 31 to 34. Pergamon Press Ltd. Printed in Northern Ireland

THE CHEMISTRY OF PERMALEIC ACID

R. W. WHITE and W. D. EMMONS
Research Laboratory, Rohm and Haas Co., Philadelphia 37, Pa.

(*Received* 15 *January* 1961)

Abstract—The preparation and reactivity of permaleic acid have been investigated, and its utility as an oxidizing agent has been demonstrated.

VOL. 17 1962

ALTHOUGH many organic peracids are well known and have been well characterized,[1] no report of the preparation or utility of permaleic acid has appeared in the literature. We have found that solutions of permaleic acid (I), prepared from maleic anhydride and hydrogen peroxide in an inert solvent,

$$C_4H_2O_3 + H_2O_2 \rightarrow HOOC{-}CH{=}CH{-}CO_3H$$

provide a very convenient and occasionally superior means for the oxidation of

(1) ketones to esters (the Baeyer-Villiger reaction)
(2) negatively substituted and simple anilines to the corresponding aromatic nitro compounds.
(3) certain olefins to epoxides.

Previously it has been possible to effect most of these oxidations using either peracetic, perbenzoic, or perphthalic acid or the more recently developed trifluoroperacetic acid.[2] However, all of the older methods suffer from disadvantages; trifluoroperacetic acid must often be used in a solvent system which is strongly buffered by inorganic salts while the other peracids are quite slow in some oxidations. The rate of permaleic acid oxidations is nearly as great as that of trifluoroperacetic acid, and permaleic acid may be used in a non-buffered system. A permaleic acid solution in methylene chloride is reasonably stable, decomposing to the extent of 5 per cent in 6 hours at ambient temperatures.

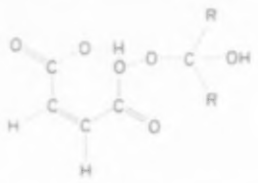
The experimental results have been summarized in Tables 1–3 along with the physical constants of the products obtained. In all cases, the constants obtained were identical to those found in the literature. The reactions were carried out by simply adding a solution of the reactant to a solution of permaleic acid in methylene chloride held at the appropriate temperature. As the reaction proceeds, maleic acid precipitates from the solution and may be removed by filtration when the oxidation is complete. The products were then isolated by conventional means.

While permaleic acid is not quite as potent a peracid as trifluoroperacetic acid, it is a much stronger oxidant than other laboratory peracids. It also has the advantage of being easily prepared and used without any intermediate transfers, and of having a reduction product which is insoluble in the media used. The solution of permaleic acid contains only 20 mole per cent maleic acid as compared to the 60–70 mole per cent of free acids in the solutions of normal peracids prepared from anhydrides and hydrogen peroxide. No external buffering system was found necessary for the oxidations

[1] D. Swern, *Org. React.* Vol. VII, 435 (1953).
[2] W. D. Emmons and G. B. Lucas, *J. Amer. Chem. Soc.* 77, 2287 (1955).

described here. The peracid was prepared and used in solution; when the concentration of permaleic acid exceeded 10–15 per cent a second heavier layer appeared. This new layer contained a larger amount of peracid than solvent, as shown by iodimetric titration, but formation of this layer did not interfere with oxidation reactions if efficient stirring was maintained.

The greater activity of permaleic acid as compared to peracetic, performic, or the aromatic peracids is attributed to the lower basicity and higher stability of the monoanion of maleic acid compared to the other acid anions. The combination of low basicity and high stability allows the electron-deficient oxygen in the transition state to be transferred to the substrate at a lower net energy cost. In the Baeyer-Villiger oxidation an additional effect may be partially responsible for the increased activity of permaleic acid since it was previously shown that the rate-determining step of this oxidation is the acid-catalyzed decomposition of the peracid-ketone complex.[3] An examination of the molecular model shows that in the transition state the acidic hydrogen on the carboxyl group of permaleic acid is in close proximity to the oxygen of the peracid grouping on which is developing a negative charge.



This autocatalysis will result in a transition state with a more favorable entropy of activation for the permaleic acid oxidation as compared to other peracids.

Ketone oxidation. The Baeyer-Villiger reaction (Table 1) has been reviewed[4] and

TABLE 1. OXIDATION OF KETONES TO ESTERS

Substrate	Time of reaction (hr)	Product	b.p.	Yield (%)
Methyl isobutyl ketone[a]	3	Isobutyl acetate	115–116°	72
Diisobutyl ketone	3	Isobutyl isovalerate	52–54° (10 mm)	83
Octanone-2	3	Hexyl acetate	56–58° (10 mm)	71
Cycloöctanone[b]	3	ω-Hydroxyoctanoic acid lactone	73–74° (9 mm)	67[b]
Estrone acetate[c]	12	Estronolactone acetate	m.p. 141–144°	40
Benzophenone	2	Phenyl benzoate	m.p. 69–70°	70
Acetophenone	2	Phenyl acetate	89–90° (17 mm)	70
Desoxybenzoin[d]	2	Benzyl benzoate		75
		Phenyl phenylacetate		

[a] Unless otherwise noted, reactions were run in methylene chloride solution at reflux, with a 70 per cent excess of peracid to ketone.

[b] An inseparable mixture of 2:1 lactone: starting ketone was formed in nearly quantitative amount. Yield based on I.R. analysis. [cf. R. Huisgen and H. Ott, *Angew. Chem.* **70**, 312 (1958)].

[c] See experimental section for details.

[d] A mixture, 75 per cent of the theoretical amount, was isolated consisting of 86 per cent benzyl benzoate and 14 per cent of phenyl phenylacetate by infrared analysis.

[3] M. F. Hawthorne and W. D. Emmons, *J. Amer. Chem. Soc.* **80**, 6398 (1958).

[4] C. H. Hassal, *Org. React.* Vol. IX, 73 (1957).

has been shown to proceed well on simple aliphatic ketones with only one oxidant, trifluoroperacetic acid, where buffering of the solution was needed to prevent transesterification of the product by the free trifluoroacetic acid. We have found that permaleic acid oxidized all classes of ketones smoothly and easily to the corresponding esters, with no noticeable transesterification of products. A greater tendency toward selective migration is noted using permaleic acid in contrast to trifluoroperacetic acid. When desoxybenzoin was subjected to the action of permaleic acid, both possible products, benzyl benzoate and phenyl phenylacetate were found, but in a 7 : 1 ratio as compared to a nearly 1 : 1 ratio when trifluoroperacetic acid was used as oxidant.[5] The greater selectivity when permaleic acid is used may be attributed to the lower reactivity of maleic acid as a leaving group when compared to trifluoroacetic acid.

VOL. 17 1962

TABLE 2. OXIDATION OF AROMATIC AMINES

Substrate	Product	m.p.	Yield (%)
p-Nitroaniline[a]	*p*-Dinitrobenzene	171–173°	87
2,4,6-Tribromoaniline	2,4,6-Tribromonitrobenzene	122–124°	90
2-Naphthylamine	2-Nitronaphthalene	77–79°	40

[a] Reactions run in CH_2Cl_2 at reflux with a 5:1 molar ratio of peracid to aniline.

The lower reactivity necessitates that the migrating group supply more driving force in the rearrangement, permitting a greater selection of the group which migrates.

Oxidation of aromatic amines. The oxidation of aromatic amines to nitro compounds using peroxyacids has been previously described.[6,7] Because of the experimentally simple techniques, permaleic acid may serve to supplement and extend this reaction (Table 2). The oxidation of 2-naphthylamine to 2-nitronaphthalene using peracids has not been reported; when trifluoroperacetic acid was used as oxidant, overoxidation occured with formation of phenolic products. If permaleic acid is used a 40 per cent yield of 2-nitronaphthalene is obtained. Unsubstituted and negatively substituted anilines quickly and easily yielded the corresponding nitrocompounds in high yield, while anilines with strongly electron donating groups were themselves overoxidized to phenolic products by permaleic acid.

Epoxidation. The olefinic link in the permaleic acid molecule is not subject to attack by the reagent itself. Internal olefins such as 9-nonadecene or 1-methylcyclohexene reacted extremely rapidly with permaleic acid at 0° but no oxirane could be isolated. Instead only products which can be derived from an acid-catalyzed attack on the intermediate epoxide such as ketones or diol monomaleates were isolated. No search for buffering conditions to prevent this facile ring-opening was made. If the double bond is deactivated by being in a terminal position or by conjugation epoxidation was possible with no buffer system (Table 3). Thus at 0° octene-1 yielded octene-1 oxide in 80 per cent yield, while at 25° only a 40 per cent yield was obtained along with a large amount of diol monoester. Methyl α-methyl glycidate could be prepared in 74 per cent yield by epoxidation of methyl methacrylate. It should be noted that the oxidation of deactivated olefins with peracetic acid prepared by air oxidation of

[5] M. F. Hawthorne, W. D. Emmons and K. S. McCallum, *J. Amer. Chem. Soc.* **80**, 6393 (1958).
[6] J. D'Ans and A. Kneip, *Ber. Dtsch. Chem. Ges.* **48**, 1144 (1915); F. P. Greenspan *Industr. Engng. Chem.* **39**, 847 (1947); E. Bamberger and F. Tschirmer, *Ber. Dtsch. Chem. Ges.* **32**, 1675 (1899); W. D. Langley, *Org. Synth.* **22**, 44 (1942).
[7] W. D. Emmons, *J. Amer. Chem. Soc.* **79**, 5528 (1957); **76**, 3470 (1954).

TABLE 3. EPOXIDATION OF OLEFINS

Substrate	Product	b.p.	Yield (%)
Octene-1[a,b]	Octene-1 oxide	51–54° (10 mm)	80
Methyl methacrylate[c]	Methyl α-methylglycidate	50° (16 mm)	74
Ethyl acrylate[c]	Ethyl glycidate	60–62° (17 mm)	33
Diallyl sulfoxide[b,d]	Diallyl sulfone	88–90° (0·4 mm)	87

[a] All reactions run in methylene chloride with 50 per cent excess preacid.
[b] Run at 0°
[c] Run at reflux
[d] Attack of peracid occurred on the S—O rather than the olefinic link.

acetaldehyde has recently been described.[8] While this is an excellent procedure the preparation of this acetic acid-free peracetic acid requires special facilities not normally available.[9]

EXPERIMENTAL

All reactions were carried out in essentially similar fashion and typical examples are given. The usual safety precautions regarding use of highly concentrated hydrogen peroxide[10] should be rigorously observed. Methylene chloride was obtained from Merck and Co.; 90 per cent hydrogen peroxide was purchased from the Buffalo Electrochemical Co.

The preparation of isobutyl acetate from methyl isobutyl ketone. To an ice-cold stirred solution of 11·6 g (0·34 mole) of 90 per cent hydrogen peroxide and 150 ml of methylene chloride was added in one batch 39·2 g (0·4 mole) of freshly crushed maleic anhydride. When the major portion of the maleic anhydride had reacted, the solution was heated to reflux and 20 g (0·2 mole) of methyl isobutyl ketone was added in an equal volume of methylene chloride. When the theoretical amount of peracid had disappeared, as determined by iodimetric titration of aliquots the solution was cooled, and the maleic acid removed by filtration. The filtrate was washed twice with 100 cc of 10% sodium carbonate solution, once with 100 cc of 10% sodium bisulfite solution, and once with 100 cc of a saturated sodium chloride solution, and dried over magnesium sulfate. Distillation through a short Vigreaux column yielded after removal of solvent, 16·7 g (72%) of isobutyl acetate, b.p. 115–116, n_D^{25} 1·3908.

2,4,6-*Tribromonitrobenzene.* To a refluxing peracid solution prepared from 3·4 g (0·1 mole) of 90 per cent hydrogen peroxide, 12·3 g (0·125 mole) of maleic anhydride and 70 ml of methylene chloride was added a solution of 6·6 g (0·02 mole) of 2,4,6-tribromoaniline and the solution was heated at reflux for 1 hr. After a workup identical to that described above, the solvent was removed to yield 6·5 g (90%) of 2,4,6-tribromonitrobenzene, m.p. 122–124°.

Octene-1 oxide. To a peracid solution at 0° prepared from 10·2 g (0·3 mole) of 90% hydrogen peroxide, 37·3 g (0·38 mole) of maleic anhydride and 150 ml of methylene chloride, was added a mixture of 22·4 g (0·2 mole) of octene-1 in an equal volume of methylene chloride. The theoretical amount of peracid had disappeared after 1·8 hr; and the mixture was worked up as usual to give 20·4 g (80%) of octene-1 oxide, b.p. 51–54° (10 mm) n_D^{25} 1·4150.

Estronolacetone acetate. To a refluxing peracid solution, prepared from 1·36 g (40 mm) of 90% hydrogen peroxide, 4·9 g (50 mm) of maleic anhydride, and 10 ml of methylene chloride was added 3·12 g (10 mm) of estrone acetate in 5 ml of methylene chloride, and the solution refluxed overnight. The precipitated maleic acid was removed by filtration, and the filtrate washed with 10 cc each of 10% sodium hydroxide, 10% sodium carbonate, 10% sodium bisulfite, and saturated sodium chloride solution. After drying over magnesium sulfate, the solvent was removed and the reddish solid was chromatographed on 35 g of cationic alumina, grade 1 (Woelm). Elution with 150 ml of benzene yielded 1 g of recovered starting material, m.p. 118–120°; further elution with 600 ml of ether gave 900 mg (40%) of estronolactone acetate, m.p. 142–144° (lit[11] 145). Passage of 500 ml of methanol through the column removed 1·0 g of amorphous red material, whose infrared spectrum showed bands attributable to a quinoid-type structure, possibly arising from attack of the peracid on the A ring.

[8] D. L. MacPeek, P. S. Starcher and B. Phillips, *J. Amer. Chem. Soc.* **81**, 680 (1959).
[9] B. Phillips, F. C. Frostick, Jr. and P. S. Starcher, *J. Amer. Chem. Soc.* **79**, 5982 (1957).
[10] F. P. Greenspan, *Industr. Engng. Chem.* **39**, 847 (1947).
[11] R. P. Jacobsen, *J. Biol. Chem.* **171**, 61 (1947).

Tetrahedron, 1962, Vol. 17, pp. 35 to 59. Pergamon Press. Ltd. Printed in Northern Ireland

VOL. 17 1962

SOME RECENT DEVELOPMENTS IN THE PREPARATIVE PHOTOLYSIS OF ORGANIC NITRITES

A. L. NUSSBAUM and C. H. ROBINSON
Natural Products Research Department, Schering Corporation,
Bloomfield, New Jersey U.S.A.

(*Received* 28 *December* 1960)

INTRODUCTION

THE use of photochemical reactions in preparative organic chemistry[1] has increased considerably during the last twenty years. Many structures accessible only with difficulty by more conventional means have been made available by the agency of radiant energy.

One of the most common primary photochemical processes is the homolytic dissociation of an appropriate bond to give rise to two fragments each containing an unpaired electron. The subsequent fate of these free radicals determines the synthetic usefulness of such photochemical processes.

It would appear that the nitrogen-oxygen bond in organic nitrite esters is particularly susceptible to homolysis. The latter process does not necessarily have to result from photochemical activation: on the contrary, most of the literature on the decomposition of nitrites describes pyrolytic procedures. In the present review, however, special emphasis will be given to photolysis, since the fragments thereby produced are endowed with sufficient energy[2] to result in subsequent behavior not otherwise attainable.

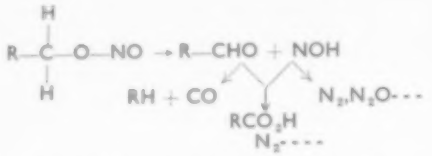
In fact, a very recent development in the field is the photolytic decomposition of nitrites to alkoxy radicals, followed by a stereoselective intramolecular hydrogen abstraction by the latter and recombination of the resulting carbon radicals with NO to form nitrose-monomers, dimers or oximes. This novel course we shall designate the *Barton Reaction*, in honor of the inventor, and experiments central and peripheral to its nature will form the core of this review.

EARLY WORK

The photochemistry of organic nitrites seems to have been investigated first by Thompson and his colleagues. Preliminary studies were reported[3] by Purkis and Thompson in 1936, and in the following year Thompson and Dainton described[4] the vapour-phase irradiation of primary, secondary, and tertiary alkyl nitrites, using both

[1] For an elegant review of the entire subject, see A. Schönberg, *Präparative Organische Photochemie*, a monograph of the series *Organische Chemie in Einzeldarstellungen* (Edited by H. Bredereck and E. Müller). Springer Verlag, Berlin, Göttingen, Heidelberg, (1958). More of a bird's eye view exists in English: A chapter entitled "Photochemical Reactions" by C. R. Masson, V. Boekelheide and W. Albert Noyes appears in *Technique of Organic Chemistry* (2nd. Ed., Edited by A. Weissberger) Vol. II. Interscience, New York (1956).
[2] See a recent article entitled "Optical Pumping" by A. L. Bloom, *Sci. Amer.* **203**, 72 (1960).
[3] C. H. Purkis and H. W. Thompson, *Trans. Faraday Soc.* **32**, 1466 (1936).
[4] H. W. Thompson and F. S. Dainton, *Trans. Faraday Soc.* **33**, 1546 (1937).

the full mercury arc and filtered radiation.[5] Their qualitative data were interpreted on the basis of decomposition to the NOH radical, together with an aldehyde, ketone or unsaturated hydrocarbon (or a combination of these):



This interpretation of nitrite photolysis differed from the mechanism which had already been proposed[6,7] for gas-phase *pyrolysis* of organic nitrites, namely O—NO fission (as the primary step) giving an alkoxy radical and NO, followed by the formation[8] of carbonyl compounds and alcohols (disproportionation)

e.g. $$RCH_2O—NO \rightarrow RCH_2O\cdot + NO$$

$$2RCH_2O\cdot \rightarrow RCHO + RCH_2OH$$

The Thompson–Dainton mechanism for nitrite photolysis remained untested for eleven years until Coe and Doumani[9] re-investigated the vapor phase photolysis of t-butyl nitrite, using a mass spectrometer for analysis of the gaseous products. The initial decomposition products, acetone and nitrosomethane,[10] were accounted for by a primary dissociation as shown:

$$(CH_3)_3C—ONO \rightarrow (CH_3)_2CO + CH_3NO$$

Not only is the production of acetone and nitrosomethane at variance with the mechanism originally[4] proposed for nitrite photolysis, but the products required by that mechanism were shown to be absent by mass spectrometric analysis.

In 1952, Gray and Style[11] examined the photolysis of methyl nitrite over a wide temperature range, using filtered mercury vapor radiation, and proposed, as the primary step, O—NO fission analogous with the Steacie mechanism for nitrite pyrolysis.

A more extensive investigation,[12] reported by Tarte, involved the photolysis of primary, secondary and tertiary alkyl nitrites. Two decomposition mechanisms were considered. The first, like the proposal of Gray and Style, requires O—NO homolysis as the initiating step. Nitrosoalkanes can then be formed either through recombination or secondary reactions between radicals and other nitrite molecules.

The alternative pathway (preferred by Tarte) is identical to that suggested by Coe and Doumani and invokes molecular rearrangement leading *directly* to nitrosoalkanes

[5] The filtered radiation consisted of the 3650, 3655 and 3663 Å triplet, which is absorbed by the nitrite group but should not lead to subsequent photolysis of ketonic and aldehydic reaction products.
[6] E. W. R. Steacie and G. T. Shaw, *J. Chem. Phys.* **2**, 345 (1934) and subsequent papers. See also E. W. R. Steacie, *Atomic and Free Radical Reactions* (2nd Ed.) Vol. I, p. 239. Reinhold, New York (1954).
[7] F. O. Rice and E. L. Radowskas, *J. Amer. Chem. Soc.* **57**, 350 (1935).
[8] These pyrolysis studies were confined to primary and secondary lower alkyl nitrites. Subsequent investigations have encompassed the pyrolysis of both tertiary and higher molecular weight alkyl nitrites, and it is now recognized that alkyl radicals and nitrosoalkanes also result from such pyrolyses. See P. Gray, P. Rathbone and A. Williams, *J. Chem. Soc.* 3932 (1960) for a summary of the recent literature on nitrite pyrolyses.
[9] C. S. Coe and T. F. Doumani, *J. Amer. Chem. Soc.* **70**, 1516 (1948).
[10] Rapid dimerization of the nitrosomethane was observed.
[11] J. A. Gray and D. W. G. Style, *Trans Faraday Soc.* **48**, 1137 (1952).
[12] P. Tarte, *Bull. Soc. Roy. Sci. Liège* **22**, 226 (1953)

and carbonyl compounds. The latter workers had objected to the existence of methyl free radicals in the photolysis of t-butyl nitrite because of the absence of detectable amounts of ethane.

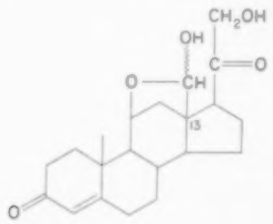
Gowenlock and Trotman[13] also scrutinized the gas phase photolytic decomposition of alkyl nitrites. Their product analysis was limited to ultraviolet absorption measurements which showed that nitrosoalkanes[14] were formed in low yield. Because these workers were particularly interested in the latter class of compounds and because of accompanying oxime formation their photolysis studies were not continued.

The photochemical investigations surveyed above have provided two reaction pathways. These two apparently distinct interpretations—i.e. intramolecular decomposition with direct generation of nitrosoalkane and a carbonyl compound vs. initial homolysis of the O—NO bond to give an alkoxy radical and NO—may be reconciled by postulating the following state of affairs: the nitrite does indeed suffer homolysis, and the resulting alkoxy radical may undergo rapid decay to give a carbonyl fragment and an alkyl radical. The latter, however, immediately combines with NO which is in close proximity to it, in preference to the alternative recombination with a more distant second alkyl radical. At any rate, nitrite photolyses are now believed to involve alkoxy radicals, and a substantial body of recent work[15] supports this point of view.

THE ALDOSTERONE PROBLEM

The current interest in nitrite photolysis which occasioned this essay arose from the application of such a photolysis to an efficient partial synthesis of aldosterone. This is not the first time that a preparative method of organic chemistry has found a fruitful area of development in the field of steroids: the use of N-bromosuccinimide[16] and of manganese dioxide[17] are notable examples of a similar nature; the importance of the steroids in biology and the advanced development of physical and chemical methods in structure correlation have made this class of compounds a favored proving ground for a variety of novel, or heretofore obscure, chemical transformations.

The powerful salt-retaining hormone of the adrenal cortex, aldosterone (I), differs from the great majority of steroids found in nature by virtue of oxygenation of the



I

angular methyl group at C-13. This substituent exists in the form of a masked aldehyde.

[13] B. G. Gowenlock and J. Trotman, *J. Chem. Soc.* 4190 (1955); 1670 (1956).
[14] The nitrosoalkanes produced by photolysis were assumed to be the same (on the basis of ultraviolet absorption maxima) as those formed by pyrolysis of the same nitrites.
[15] See P. Gray and A. Williams, *Chem. Rev.* **59**, 239 (1959).
[16] C. Djerassi, *Chem. Rev.* **43**, 271 (1948).
[17] R. M. Evans, *Quart. Rev.* **13**, 61 (1957).

In order to arrive at a synthesis of such a structure, the following approaches have been utilized:[18]

(A) Total synthesis from simple, non-steroidal starting materials. This requires resolution of a racemic mixture.

(B) Fission of ring D of a steroid precursor devoid of C-18 oxygenation, introduction of a desired substituent into an angular methyl group temporarily activated by adjacent substitution, followed by reconstitution of ring D. The latter operation has been beset by great difficulties.

(C) Utilization of naturally occuring steroidal structures already possessing functional substituents at the C-18 angular methyl group.

(D) Oxygenation of C-18 by enzymatic means.

(E) Novel chemical means duplicating this enzymatic selectivity for an isolated, non-activated angular methyl group.

For a variety of reasons, the last-named approach has proved to be the one by means of which a great portion of the available synthetic aldosterone has actually been synthesized. The problem, as stated in the review mentioned above,[18] was to find "neuartige partialsynthetische Methoden, die auf einer breiten Base eine direkte und selektive Substitution der reaktionsträgen Methylgruppe 18 von intakten Steroiden erlauben". A number of such methods have, in fact, been recently developed.

In general, means were chosen to generate a highly reactive species (free radical, diradical such as uncoupled carbonyl, carbene, or a cationic species such as RO^+) of high energy content, which was located close in space to the methyl group, thus permitting the desired direct and selective attack. These methods included the Hofmann–Löffler–Freytag reaction (transforming 20-amino compounds to conane derivatives), generation of carbene at C-21 via diazoketone with subsequent attack on C-18, photochemical cyclization by the irradiation of C-20 ketones and, most fruitfully, formation of 18,20-ether linkages by the action of lead tetraacetate on 20-hydroxy compounds. The more important factors which should be considered in reactions of the general type described are (1) availability of starting material, (2) specificity of the reaction for the desired site—i.e. the reaction should tolerate the presence of a variety of non-interfering functional groups in the molecule, thus permitting a short synthetic sequence, and (3) efficiency of the process selected to assure a high degree of conversion to the desired product.

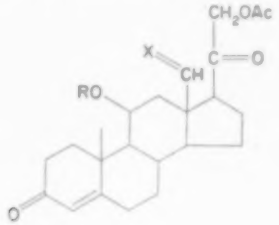
These considerations led D. H. R. Barton to select nitrite photolysis as a potentially useful tool for the general end in view. As can be seen from the discussion above, nitrites are a good source of alkoxy radicals. Generation of such an alkoxy radical, suitably located within the framework of the relatively rigid steroid molecule, might result in intramolecular hydrogen abstraction from a preselected site. (The excited energy state of the alkoxide radical, as guaranteed by its photolytic origin, might make such abstraction predominate over the relatively trivial disproportionation to the ketone). The resulting carbon free radical would then decay in a characteristic manner and, depending which of the various possibilities were to predominate, might be useful in such special aims as aldosterone synthesis.

The experimental work, carried out at the Research Institute of Medicine and Chemistry (RIMAC) in Cambridge, Massachusetts, demonstrated that nitrite

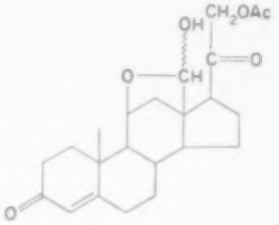
[18] This subject has been ably reviewed in a recent article by K. Schaffner, D. Arigoni and O. Jeger, *Experientia* **16**, 169 (1960), which should be consulted for leading references.

photolysis did indeed result in intramolecular hydrogen abstraction from a desired site. Moreover, the resulting free radical underwent chain termination by recombination with NO, presumably the very NO generated by the original photolysis, to form the derived nitroso derivative isolated as the oxime. Thus, direct introduction of functionality into an unactivated position had been achieved; a functionality, moreover, which could be easily converted to an aldehyde or a variety of other chemical structures.

As applied specifically to the synthesis of aldosterone 21-acetate,[19] this involved the conversion of corticosterone acetate (2, R=H, X=H_2) to its nitrite (2, R=NO, X=H_2). Irradiation of the latter caused precipitation of aldosterone acetate oxime



2



3

(2, R=H, X=NOH) which was hydrolyzed to the desired aldosterone acetate (3) with nitrous acid.

RECENT DEVELOPMENTS

The remainder of this review will be devoted to a description of experiments which have been carried out at RIMAC and in the laboratories of the Schering Corporation with the aim of exploiting the Barton Reaction and delineating its scope. If nitrite photolysis does indeed give rise to alkoxide free radicals, then it would be useful to consider the following reactions from the point of view of alkoxide radical, chemistry,[15] and we find it convenient to use the classification of Gray and Williams, as outlined in their excellent review. According to these authors, alkoxide radicals may react by any of the following pathways:

(1) Association with other radicals, including dimerization.
(2) Addition to unsaturated compounds.
(3) Hydrogen abstraction from another molecule.
(4) Disproportionation.
(5) Rearrangement, including internal hydrogen abstraction.
(6) Decomposition by carbon or hydrogen elimination.

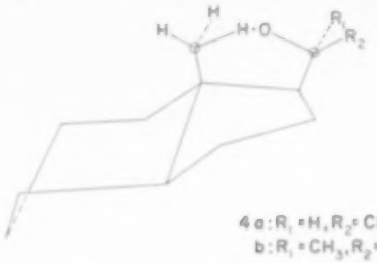
Several of these pathways have been observed in nitrite photolysis and have already been described: we shall deal with others in due course.

The Barton Reaction is clearly an example of intramolecular hydrogen abstraction. Energetically, this is not a favored step, since "C—H bond fission is expected to play only a minor role in the decomposition of alkoxyl radicals."[20] However, the energy is not the only factor to be considered. McBay and Tucker[21] enumerate, in addition, a steric and a repulsion factor; clearly, the steric factor must play a very considerable role in the Barton Reaction, and in any case, the photolytic origin of the presumed

[19] D. H. R. Barton and J. M. Beaton, *J. Amer. Chem. Soc.* **82**, 2641 (1960).
[20] See ref. 15, p. 276.
[21] H. C. McBay and O. Tucker, *J. Org. Chem.* **19**, 869 (1954).

alkoxy radical, because of the high energy content of the latter, would be expected to facilitate pathways otherwise thermodynamically unfavorable.

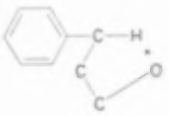
A more detailed consideration of the steric factors involved in intramolecular hydrogen abstraction suggest the existence of a six-membered transition state (4).



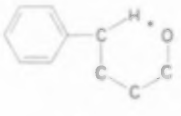
4 a: $R_1 = H, R_2 = CH_3$
b: $R_1 = CH_3, R_2 = H$

Structures of this type were first proposed by Davis and Noyes[22] in connection with the irradiation of ketones, and have recently been discussed by Yang[23] and the Swiss authors previously quoted.[18] Such a concept would predict attack on the hydrogen of a carbon atom removed by two from that holding the active abstractor, a course which is actually observed. Incidentally, a transition state as pictured in 4 would also help to explain the observation[24] that the yield of 18-oxime from a 20α-nitrite is much higher than from the corresponding 20β-isomer: examination of the model (4) shows that the proposed transition state of the former (a) is sterically preferable to the latter (b), since in 4a the bulkier methyl group points away from the rest of the molecule, whereas in 4b distinct hindrance with the rear of the steroid molecule, especially at C-12, is manifestly observed.[25]

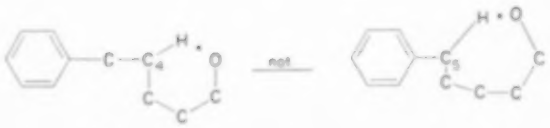
Conclusive support for the formation of a six-membered transition state in the Barton Reaction comes from the work of Kabasakalian *et al.*[26] who studied the photolysis of aromatic alkyl nitrites in solution. 3-Phenyl-1-propyl nitrite did not give rise



5



6



7 8

[22] W. Davis, Jr. and W. A. Noyes, Jr., *J. Amer. Chem. Soc.* **69**, 2153 (1947).
[23] N. C. Yang and D. D. H. Yang, *J. Amer. Chem. Soc.* **80**, 2913 (1958).
[24] A. L. Nussbaum, F. E. Carlon, E. P. Oliveto, E. Townley, P. Kabasakalian and D. H. R. Barton, *J. Amer. Chem. Soc.* **82**, 2973 (1960).
[25] L. Velluz, G. Muller, R. Bardoneschi and A. Poittevin, *C. R. Acad. Sci., Paris* 725 (1960), in a reaction which generates a C18 → C20 ether bridge by means of lead tetraacetate and which must also involve conformational considerations of the kind here outlined, report considerably higher yields from the 20α- than from the 20β-isomer. *Note added in proof:* This has now been rationalized in a manner identical to ours. *Cf.* G. Cainello, B. Kamber, J. Keller, M. Lj. Mihailovic, D. Avigoni and O. Jeger, *Helv. Chim. Acta* **44**, 518 (1961).
[26] P. Kabasakalian, E. R. Townley and M. D. Yudis, in preparation.

to any nitroso dimer: the postulated 5-membered ring transition state (5) apparently did not form, in spite of the predicted ease of benzyl–hydrogen abstraction. 4-Phenyl-1-butyl nitrite can form a six-membered transition state (6) and isolation of the corresponding nitroso-dimer supports this view. A particularly intriguing instance is the next higher homologue, 5-phenyl-1 pentyl nitrite. This compound undergoes hydrogen abstraction at C-4 (7) rather than C-5 (8); apparently the advantages to be gained from a six-membered vs. a seven-membered complex outweigh the greater ease of benzyl–hydrogen abstraction.

We shall now proceed to enumerate systematically the results so far obtained in an investigation of the Barton Reaction.

VOL. 17 1962

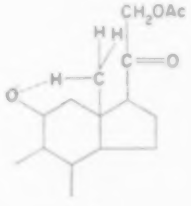
I. INTRAMOLECULAR HYDROGEN ABSTRACTION

A. *Termination with* NO

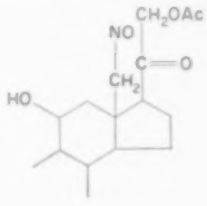
1. *Formation of oxime*

The recombination of a carbon radical with NO is not unprecedented: NO is a well-known radical trap.[27] The resulting monomeric nitroso compound may then dimerize (see next section) or rearrange to the oxime. Such recombinations have been observed for a large number of cases, the mode of alkyl radical generation ranging ranging anywhere from the thermal decomposition of peroxides[28] or alkyl mercury derivatives[29] to the direct irradiation of certain organic compounds by means of γ-rays.[30] The process in which alkyl free radicals are generated by irradiation of hydrocarbons in the presence of nitrosyl chloride to give oximes was first described by Lynn,[31] and this and related procedures have been investigated in great detail by Müller and his school;[32] eventually an economically important synthesis of cyclohexanone oxime resulted.

The Barton Reaction proper was first applied to steroids, as has already been discussed. In the aldosterone synthesis,[19] hydrogen at C-18 is abstracted by an alkoxy radical at C-11β: the six-membered transition state 9 appears convincing. The postulated intermediate nitroso-monomer 10 resulting from recombination of the C-18



9

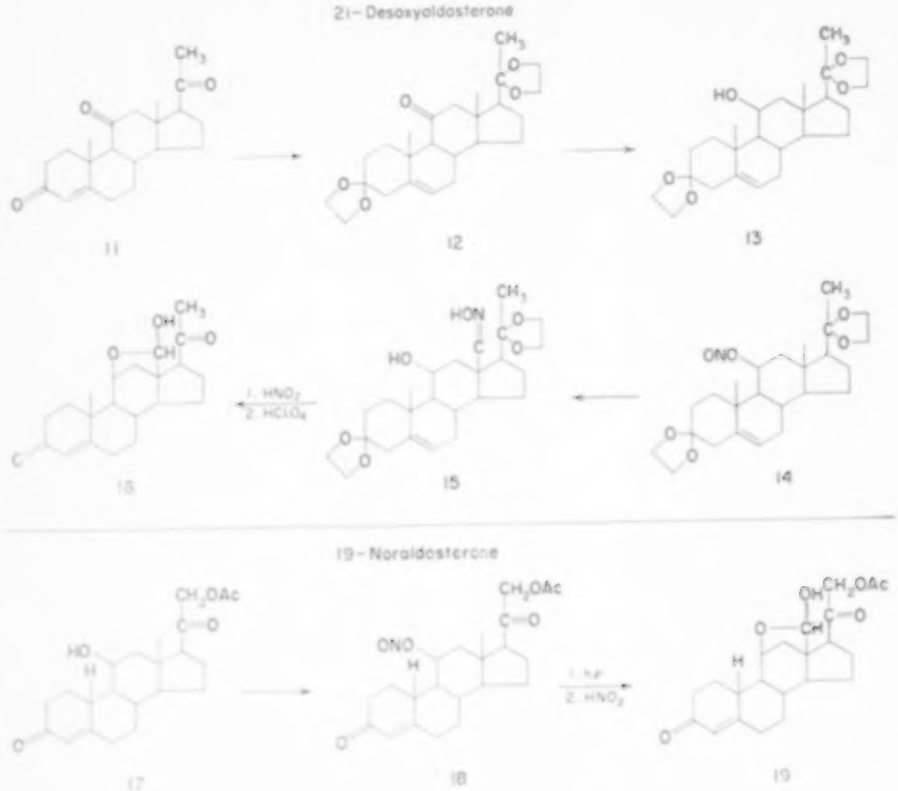


10

radical with NO does not dimerize, presumably because steric factors prevent the convergence of two steroid molecules, but rearranges to the oxime (2, X = NOH) instead.

[27] See N. N. Semenov, *Angew. Chem.* **69**, 775 (1957); C. N. Hinshelwood, *Ibid.* **69**, 446 (1957).
[28] J. H. Raley, F. F. Rust and W. E. Vaughan. *J. Amer. Chem. Soc.* **70**, 88 (1948).
[29] W. A. Bryce and K. U. Ingold, *J. Chem. Phys.* **23**, 1968 (1955).
[30] A. Henglein, *Angew. Chem.* **72**, 603 (1960).
[31] E. V. Lynn, *J. Amer. Chem. Soc.* **41**, 368 (1919) and later publications.
[32] E. Müller, H. Metzger, D. Fries, V. Heuschkel, K. Witte, E. Waidelich and G. Schmid, *Angew. Chem*, **71**, 229 (1959).

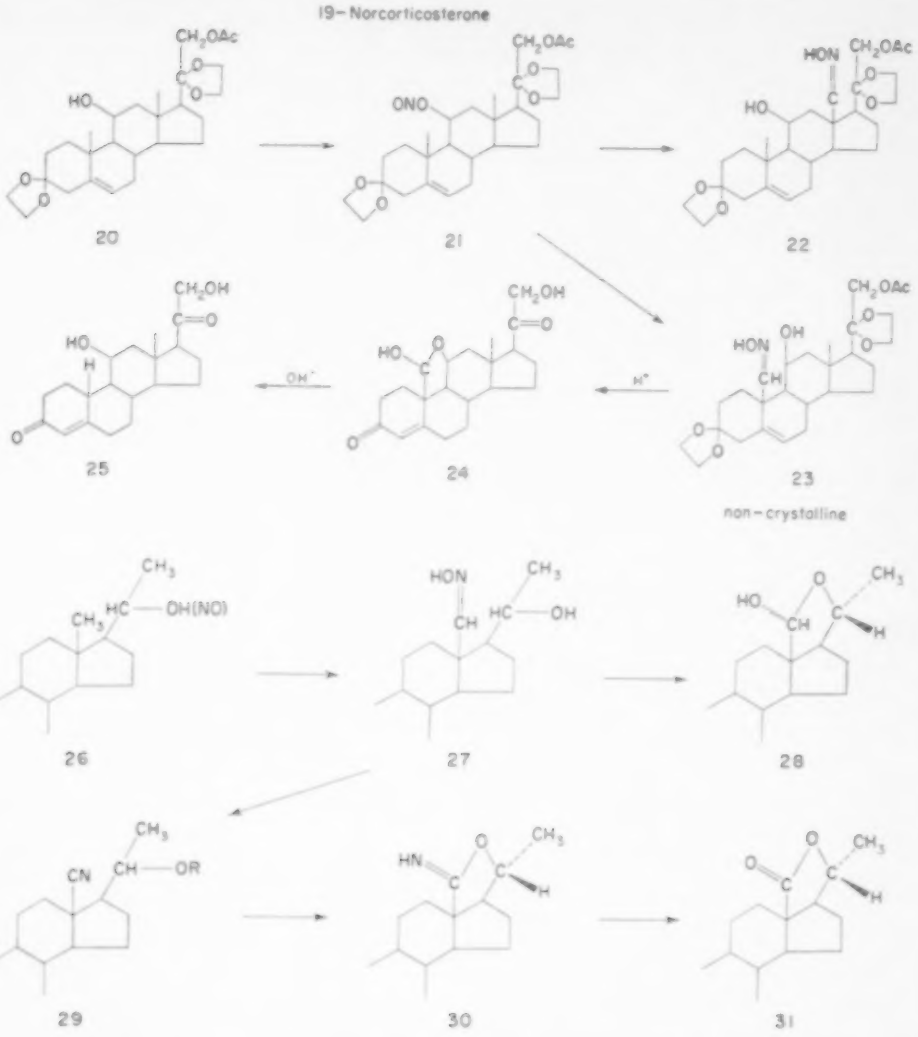
Subsequently, this general procedure of attack at C-18 via the 11-nitrite was broadened and resulted in the synthesis of 21-desoxyaldosterone[33] (11–16) and 19-noraldosterone.[34] (17–19) Both syntheses are outlined in flow-sheet form.



Incidentally, irradiation of steroidal 11β-nitrites does not necessarily result in exclusive attack at C-18: hydrogen abstraction from the other angular methyl group may result, as well; the 19-norcorticosterone used as a precursor (in form of its acetate) for 19-noraldosterone (17) arose from such a course.[34] Corticosterone 3,20-bisethyleneketal[35] was acetylated (20) and converted to the 11β-nitrite (21), which upon irradiation gave both the 18-oxime (22) and a non-crystalline 19-oxime (23). The latter, upon treatment with acid, gave the 19-isomer of aldosterone (24). Alkali treatment resulted in a retro-aldol elimination[36] to the known[37] 19-norcorticosterone (25).

Attack at C-18 is also possible from alkoxide radical at C-20. In their original

[33] A. L. Nussbaum, G. Brabazon Topliss and E. P. Oliveto, unpublished data.
[34] D. H. R. Barton and J. M. Beaton, *J. Amer. Chem. Soc.* **83**, 750 (1961).
[35] S. Bernstein and R. H. Lenhard, *J. Amer. Chem. Soc.* **77**, 2331 (1955).
[36] *Cf* D. H. R. Barton and P. DeMayo, *J. Chem. Soc.* 887 (1953). See esp. A. S. Meyer, *Experientia* **11**, 99 (1955).
[37] A. Zaffaroni, H. J. Ringold, G. Rosenkranz, F. Sondheimer, G. H. Thomas and C. Djerassi, *J. Amer. Chem. Soc.* **80**, 6110 (1958).



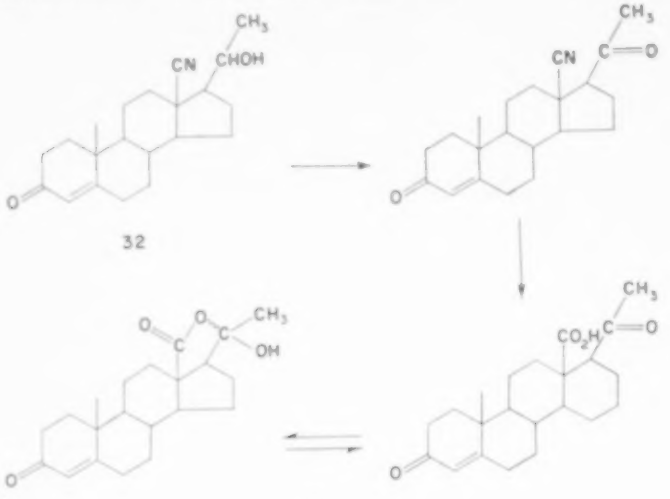
communication, Barton and co-workers[38] report such an attack and subsequent transformations as outlined (26–31).

The especially strategic location of substituents at C-20 for attack on the C-18 angular methyl group has, of course, been noted with a variety of other reactions[18] (*vide supra*). It was pointed out recently, however, that slight changes in bond angles (brought about by a trigonal C-11, for instance) might result in sufficient deformation of the molecule to vitiate the desired hydrogen abstraction.[39]

Incidentally, when the approach outlined (26–31) was carried out in the progesterone series, it was possible to prepare a number of substances useful in correlating several

[38] D. H. R. Barton, J. M. Beaton, L. E. Geller and M. M. Pechet, *J. Amer. Chem. Soc.* **82**, 2640 (1960).
[38a] The photolysis products described in this review article are indeed the result of light-induced reactions rather than of thermal decomposition: this was ascertained by performing the necessary controls.
[39] A. Bowers and E. Denot, *J. Amer. Chem. Soc.* **83**, 4956 (1960).

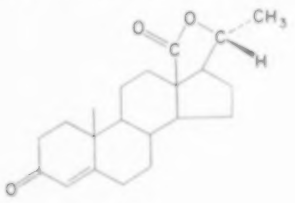
independent lines of inquiry. Thus, oxidation and acid hydrolysis of the nitrile 32 (analogous to 29) gave rise to 3,20-diketo-4-pregnen-18-oic[24] acid 33 identical with a material derived from the steroidal alkaloid conessine.[40]



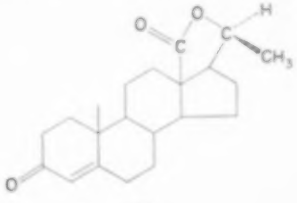
32

33

Similarly, hydrolysis and oxidation of the progesterone analogue of 27 (20β) gave the 20β-lactone 34, identical with a substance derived from holarrhimine.[41] Finally a



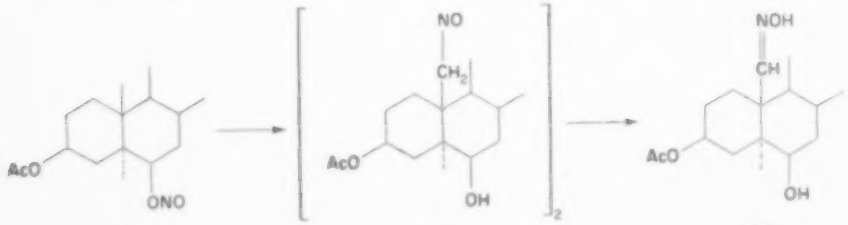
34



35

corresponding hydrolytic oxidation of the isomeric 20α-oxime led to the 20α-lactone 35 also derived from paravallarine.[42,43]

A third position in the steroid molecule investigated as to the course of nitrite



36 37 38

[40] R. Pappo, *J. Amer. Chem. Soc.* **81**, 1011 (1959).

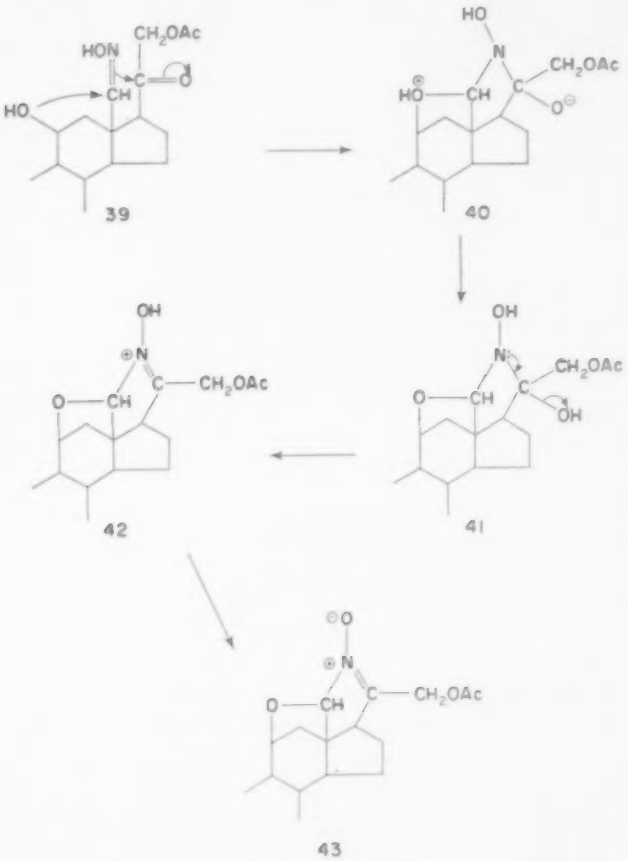
[41] L. Lábler and F. Šorm, *Chem & Ind.* 935 (1960).

[42] J. LeMen, *Bull. Soc. Chim. (Fr.)* 860 (1960).

[43] Here, too, one of us (A.L.N.) wishes to thank Drs. Pappo and Lábler and Prof. LeMen for their kindness in either providing samples or carrying out the necessary comparison.

photolysis was C-6β.[38] The nitrite derived from cholestane-3β,6β-diol 3-acetate (partial 36) was irradiated,[38a] and the resulting nitroso dimer 37 (see below) was converted to the 19-oxime 38 by refluxing in 2-propanol. In this instance, as in all those preceding, a six-membered transition state would seem to be required for internal hydrogen abstraction.

As was stated earlier, the primary product of the Barton Reaction is considered to be a nitroso compound, which may either dimerize (see next section) or rearrange to the oxime. The latter substance, however, may itself react further under the proper



circumstances. Thus, an examination[43a] of the mother liquors of the aldosterone 18-oxime obtained from the irradiation of corticosterone acetate 11-nitrite[19] (2, R = NO, X = H_2) showed the presence of nitrone; the latter was also obtained by thermal treatment or refluxing in methanol, of the oxime.[19] This transformation is pictured in 39–43:[43b]

[43a] J. M. Beaton, personal communication.

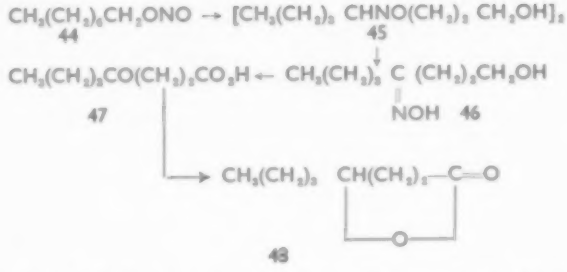
[43b] For nitrone formation from nitroso compounds, see W. J. Hickinbottom, *The Chemistry of Carbon Compounds* (Edited by E. H. Rodd) Vol. IIIA, p. 151. Elsevier, Amsterdam (1954).

2. *Formation of nitroso dimer*

Attention has already been called to the fact that the postulated monomeric nitroso compound resulting from the Barton Reaction may dimerize (see preceding section). An instance of this kind in the steroid series has been reported (vide supra, 37).

In the absence of steric factors unfavorable to dimerization of the intermediate mononitroso precursors, dimerization is indeed widely observed. P. Kabasakalian and his co-workers of these Laboratories have recently begun a detailed study of the photolysis of simple organic nitrite esters. In contrast to earlier work, their experiments were carried out in solution: this would presumably favor the Barton Reaction and interaction with solvent molecules. Rigorous qualitative identification of reaction products was carried out in many cases; in others, quantitative estimation by ultraviolet spectrometry was employed.

As an initial study,[44] the photochemistry of n-octyl nitrite (44) was investigated. When the reaction was carried out in heptane (no oxygen present), the principal product was found to be the dimer of 4-nitroso-1-octanol (45). The latter was thermally isomerized to oxime 46, which was oxidized and hydrolyzed to 4-ketoöctanoic



acid (47). Reduction of the ketone gave a hydroxyacid convertible to the γ-lactone (48). These transformation products were known compounds[45] which had been prepared earlier in these same Laboratories.

No substitution in any but the 4-position could be observed: this strongly supports the concept of a six-membered cyclic transition state. The notion that the initial step is dissociation of the nitrite to alkoxy radical and NO is buttressed by the finding that the addition of excess NO drastically reduces the quantum yield of the reaction: the reverse of the dissociation 44 to 49 would result in just that.

The photochemistry of certain aromatic alkyl nitrites[26] has already been discussed (*vide supra*).

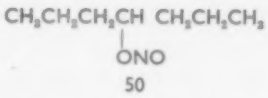
An examination of the yield of nitroso-dimers from photolysis of a variety of nitrites of diverse structure[46] led to the following observations:

(a) The Barton Reaction, leading to nitroso-dimers, always requires a six-membered ring transition state.

(b) Yields of nitroso-dimer[47] drop sharply when the hydrogen to be abstracted

[44] P. Kabasakalian and E. R. Townley, *J. Amer. Chem. Soc.* In press.
[45] D. Papa, E. Schwenk and H. Ginsberg, *J. Org. Chem.* **14**, 726 (1949).
[46] P. Kabasakalian, E. R. Townley and M. D. Yudis, *J. Amer. Chem. Soc.* In press.
[47] As determined by ultraviolet analysis; molar absorptivity of pure nitroso dimer is ca. 9500.

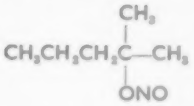
intramolecularly is primary rather than secondary or tertiary. (This drop is partially offset in the case of 4-heptyl nitrite (50), where the statistical availability of two



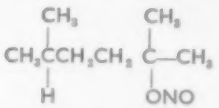
50

primary hydrogens provides compensation.) This is in accordance with the greater energy requirements of primary C—H bond rupture.[15]

(c) Nitroso-dimers may also be obtained by pathways different from the Barton Reaction, i.e. C—C bond fission (*vide infra*). This is apparent from product analysis, and begins to show up for some secondary nitrites. In the case of certain tertiary nitrites (i.e. where the hydrogen to be abstracted is primary), such competing pathways may operate. For example, 2-methyl-2-pentyl nitrite (51) does not readily undergo the



51



52

Barton Reaction, whereas 2,5-dimethyl-2-hexyl-nitrite (52) does so in good yield.[48]

It should be pointed out that no nitroso dimers were obtained in the photolysis *in solution* of t-butyl, 1-propyl and ethyl nitrites. This is in contrast to earlier work[4,9,12,13] carried out in the *vapor phase*.

In addition to the application of the Barton Reaction to aliphatic, aromatic and steroidal compounds, this method has also been applied to a variety of special classes of substances. Tables 1 and 2 list two of these[49] together with the absorptivities due to the nitroso-dimers.

TABLE 1. NITROSO-DIMER FORMATION WITH SEVERAL ISOPRENOID NITRITES

Nitrite	a^{*}_{max}	λ
Farnesol	2000	288
Geraniol	2000	292
Menthol	4800	290
Citronellol	2700	294
Nerol	2800	294

* a_{max} ~9500 (for pure nitroso-dimer).

TABLE 2. NITROSO-DIMER FORMATION FROM NITRITES OF SOME FATTY ALCOHOLS

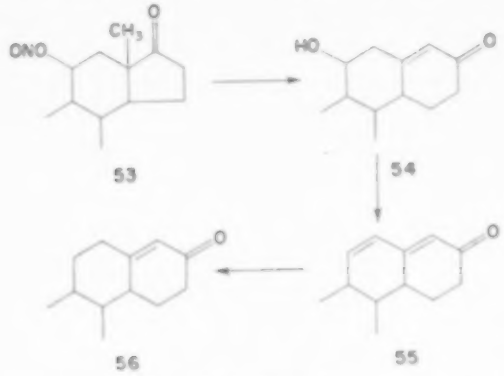
Nitrite	% Nitroso-dimer by U.V.
Dodecanol	29·2
Tetradecanol	37·2
Hexadecanol	55·2
Octadecanol	33·0

[48] The product of the Barton Reaction in this case is actually the 5-nitroso monomer. This seems to be generally true when tertiary hydrogens are abstracted.

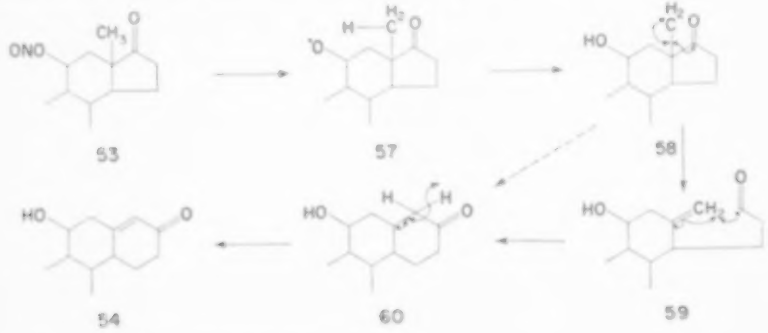
[49] P. Kabasakalian, unpublished work.

B. *Alkyl Radical Intermediate Rearrangement with* C-C *Fission: Termination by Loss of* H-*Atom*

We come now to a case which starts out as a typical Barton Reaction—a carbon radical is formed via the usual intramolecular hydrogen abstraction in the six-membered cyclic transition state—but the resulting alkyl radical does not recombine with NO: instead, a rearrangement takes place. Partial structure (53), when irradiated in toluene,[50] gave an α,β-unsaturated ketone which turned out to be the 18-nor-D-homosteroid (54), as proved by conversion to (55) and hydrogenation to the known 56.[51]



Sequence 53 to 54 is rationalized in the following manner:



(Arrows indicate single electron movements).

This mechanism is strengthened by writing the structure as depicted in partial formula (59): such relatively stable radicals have been implicated in the autoöxidation of benzaldehyde, etc.[52]

A possible alternative view would be the direct rearrangement (58) to (60).

The free radical rearrangement recently reported[53] as formally of the Wagner–Meerwein type would seen to be another example of the same order as the one here described.

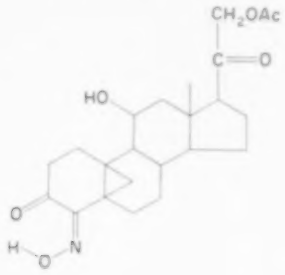
[50] H. Reimann, A. S. Capomaggi, T. Strauss, E. P. Oliveto and D. H. R. Barton, *J. Amer. Chem. Soc.* In press.
[51] The actual compound was 18-nor-D-homo-4,13(17a)-androstadiene-3,17-dione. See H. Heusser, J. Wohlfahrt, M. Müller and R. Anliker, *Helv. Chim. Acta* **42**, 2140 (1959).
[52] W. A. Waters, *Physical Aspects of Organic Chemistry* (4th Ed.), p. 196. Van Nostrand, New York (1950).
[53] J. A. Berson, C. J. Olsen and J. Singh Walia, *J. Amer. Chem. Soc.* **82**, 5000 (1960).

VOL. 17 1962

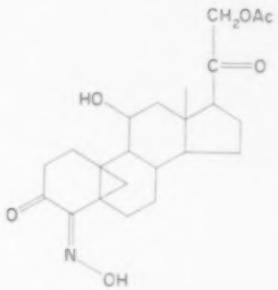
C. *Alkyl Radical Intermediate Rearrangement by Addition to an α,β-Unsaturated Ketone*

Another case commencing by intramolecular hydrogen abstraction but terminating by a path other than immediate recombination with NO has been encountered during nitrite photolysis.

Further examination[43a] of the mother liquors from the irradiation of corticosterone acetone nitrite[19] (2, R = HO, X = H_2)—already shown to contain nitrone 43—yielded two additional products which, on the basis of subsequent structure elucidation work, were formulated as the α-oximinoketones 61 and 62.

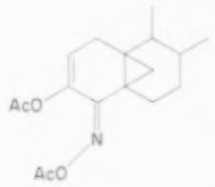


61



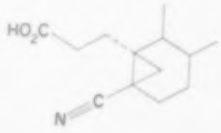
62

For detailed discussion, the original paper should be consulted, but some of the salient points may be mentioned. The less polar 61 could be converted to 62 by heat. Absence of the typical spectroscopic features of Δ^4-3-ones implicated ring A of the molecule. Consideration of the ultraviolet spectra permits the *syn* and *anti* assignments as shown, by analogy with the corresponding benzil monoximes, and infrared data support the assignment. Mild acetylation of 61 gave structure 63 with its rather



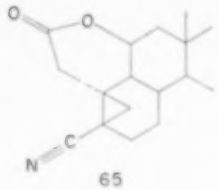
63

typical behavior in the ultraviolet, whereas 62 underwent a second order Beckmann rearrangement, giving rise to a nitrilo-acid formulated as in 64. (Nitrile absorption is modified by conjugation with the cyclopropane ring.) This acid was also obtained



64

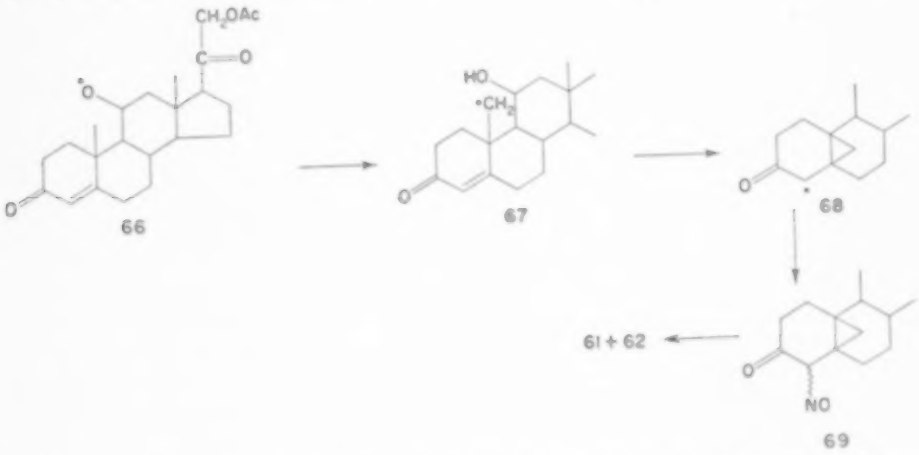
from both monoximes by use of $POCl_3$/pyridine. A slight change in the workup[54] gave instead a nitrilolactone, 65



65

The origin of these two keto-monoximes, 61 and 62, can be rationalized as follows:[55]

The alkoxide radical 66 abstracts a hydrogen atom from the C-19 angular methyl group to give the alkyl radical 67. The latter adds to the α,β-unsaturated system of



66 67 68 69

Ring A to generate another alkyl radical (68) having the unpaired electron at C-4. Recombination with NO gives 69 which rearranges to the two isonitroso derivatives 61 and 62.

Just as the foregoing rearrangement was considered formally analogous to that of Wagner–Meerwein, the rearrangement here discussed bears a corresponding resemblance to the Michael addition.

II. INTERMOLECULAR HYDROGEN ABSTRACTION

A commonly encountered product in the liquid-phase photolysis of a host of organic nitrites has been the corresponding alcohol. The propensity of alkoxy radicals for abstracting hydrogen from other molecules (e.g. solvent) is well documented,[56] and *inter*molecular hydrogen abstraction can be expected to compete with the *intra*molecular mode of hydrogen transfer (Section I) and indeed with all the decay reactions of an alkoxy radical:

$$R\text{—}O\cdot + XH \text{ (e.g. solvent)} \rightarrow R\text{—}OH + X\cdot$$

[54] Observation by H. Reimann of these Laboratories.
[55] Private communication from Dr. J. M. Beaton, Institute for Medicine and Chemistry, Cambridge, Massachusetts.
[56] See ref. 15, pp. 267–272 for a discussion of this topic.

VOL. 17 1962

However, the extent to which this undesirable competition occurs is greatly influenced by the nature of the solvent, as will be seen below. At this point, the reservation must be made that, in the case of primary and secondary alkoxy radicals, disproportionation reactions (i.e. hydrogen transfer from one radical to another) can also lead to alcohols (and, necessarily, carbonyl compounds; see Section III A) thus:

$$2R_1R_2CH{-}O\cdot \rightarrow R_1R_2C{=}O + R_1R_2CHOH$$

Striking evidence for intermolecular hydrogen abstraction has been secured recently from detailed studies with 1-octyl nitrite.[44] Photolysis of this nitrite, in benzene solution, gave as the major product dimeric 4-nitroso-1-octanol (the genesis of this nitrosodimer has already been discussed in Section I) together with lesser amounts of 1-octanol and 1-octanal. The formation of the two last-named products can be attributed to hydrogen abstraction (A) and disproportionation processes (B) as shown:

$$CH_3(CH_2)_6CH_2ONO \rightarrow CH_3(CH_2)_6CH_2O\cdot + NO$$

$$CH_3(CH_2)_6CH_2O\cdot + XH\ (\text{solvent}) \rightarrow CH_3(CH_2)_6CH_2OH + X\cdot \quad (A)$$

$$2CH_3(CH_2)_6CH_2O\cdot \rightarrow CH_3(CH_2)_6CH_2OH + CH_3(CH_2)_6CHO \quad (B)$$

The extent to which intermolecular hydrogen abstraction occurs will depend on the efficiency of the solvent (XH) as a hydrogen donor, and indeed studies with a variety of solvents show that the highest yield of 4-nitroso-1-octanol dimer (the product of *intra*molecular hydrogen abstraction) occurs when benzene, a poor donor, is used.

With heptane as solvent, however, not only was 4-nitroso-1-octanol dimer (see Section I) formed, but other nitroso dimers were generated in appreciable quantities. These new products proved to be nitrosoheptane dimers and nitrosoheptane-4-nitroso-1-octanol *mixed dimers*. These results have been explained as follows (equations 1–6).

$$CH_3(CH_2)_6CH_2ONO \xrightarrow{h\nu} CH_3(CH_2)_6CH_2O\cdot + NO \quad (1)$$

$$CH_3(CH_2)_6CH_2O\cdot \rightarrow CH_3(\dot{C}H_2)_5CH(CH_2)_2CH_2OH \quad (2)$$

$$CH_3(CH_2)_5\dot{C}H(CH_2)_2CH_2OH + NO \rightarrow CH_3(CH_2)_5CHNO(CH_2)_2CH_2OH \quad (3)$$

Barton Reaction

$$CH_3(CH_2)_6CH_2O\cdot + CH_3(CH_2)_4CH_2CH_3 \rightarrow CH_3(CH_2)_6CH_2OH + CH_3(CH_2)_4\dot{C}HCH_3 \quad (4)$$

—intermolecular hydrogen abstraction[56a]

$$CH_3(CH_2)_4\dot{C}HCH_3 + NO \rightarrow CH_3(CH_2)_4CHNOCH_3 \rightarrow \text{dimer} \quad (5)$$

$$CH_3(CH_2)_4CHNOCH_3 + CH_3(CH_2)_5CHNO(CH_2)_2CH_2OH \rightarrow \text{mixed dimer} \quad (6)$$

The 2-nitrosoheptane formed according to equations 4 and 5 can dimerize either with another 2-nitrosoheptane molecule or with a molecule of 4-nitroso-1-octanol.

Substitution of toluene for heptane as solvent resulted (not unexpectedly) in the formation of dimeric ω-nitrosotoluene as well as 4-nitroso-1-octanol dimer.

III. DECOMPOSITION REACTIONS

A. C—H *Bond Fission*

The formation, without carbon skeleton change, of aldehydes and ketones from primary and secondary alkyl, alicyclic and aryl substituted nitrites has been widely observed:

$$RCH_2{-}ONO \xrightarrow{h\nu} RCHO$$

$$R_1R_2\ CH{-}ONO \xrightarrow{h\nu} R_1R_2CO$$

[56a] Abstraction from C-2 is here pictured. In actual fact statistical abstraction of the secondary hydrogens was observed.

These findings are conveniently explained either by alkoxy radical decomposition through loss of an α-hydrogen (e.g. equation 1) or by a disproportionation process (cf. Section II).

$$R_1R_2CH\text{—}O\cdot \rightarrow R_1R_2C\text{—}O + H\cdot \qquad (1)$$

It has deen argued[57] that C—H bond fission should not be a major factor in the decomposition of alkoxy radicals, on the assumption (by analogy with alkyl radicals and normal molecules) that C—H fission will be energetically less favoured than C—C fission.

However, the generation of alkoxy radicals in dilute solution (as in the present work) will surely suppress the alternative disproportionation mechanism. This general effect can be supplemented, in particular cases, by factors of structural origin such as steric compression (as in the case of a steroidal 11β-alkoxy radical) or the difficulty of a fruitful collision between two alkoxy radicals because of nearby bulky groups (this would be particularly true in the steroid series where nitrosodimer formation is rarely seen, presumably for similar steric reasons; see Section IA).

In cases where these factors are all operative at one and the same time, it can therefore be supposed that C—H fission will predominate over disproportionation reactions.

B. C—C *Fission*

Previous sections of this review have dealt with the Barton reaction (together with deviations which nevertheless proceed *via* intramolecular hydrogen abstraction) and trivial competing reactions—hydrogen abstraction from solvent, disproportionation, C—H fission.

We shall now consider another reaction path which frequently competes with the Barton reaction, namely alkoxy radical decomposition by C—C cleavage:

$$RCH_2O\cdot \rightarrow R\cdot + CH_2O \qquad (1)$$

$$R_1R_2CHO\cdot \rightarrow R_1\cdot + R_2CHO \text{ or } R_2\cdot + R_1CHO \qquad (2)$$

$$R_1R_2R_3CO\cdot \rightarrow R_1\cdot + R_2R_3CO \text{ or } R_2\cdot + R_1R_3CO \text{ or } R_3\cdot + R_1R_2CO \qquad (3)$$

In the case of alkoxy radicals derived from alicyclic nitrites, ring fission can occur as shown:

e.g.[58]

(4)

Specific examples for processes (1) to (4) will now be given.

1. *Primary alkoxy radical decomposition*

The surprising failure of ethyl and 1-propyl nitrites (which cannot furnish the 6-membered cyclic transition state needed for intramolecular hydrogen abstraction) to generate nitroso dimers in solution *via* C—C decomposition (equations 5–7) has already been noted [Section I A (2)].

$$R\text{—}CH_2\text{—}ONO \xrightarrow{h\nu} R\text{—}CH_2\text{—}O\cdot + NO \qquad (5)$$

$$R\text{—}CH_2\text{—}O\cdot \rightarrow R\cdot + CH_2O \qquad (6)$$

$$R\cdot + NO \rightarrow RNO \qquad (7)$$

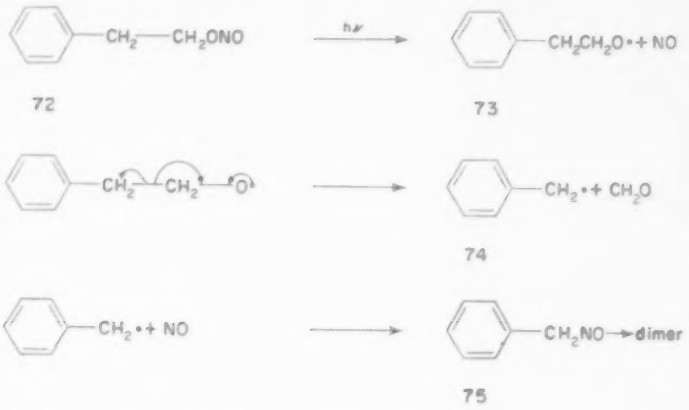
Not observed where R is H, CH_3 or C_2H_5

[57] ref. 15, pp. 275–276.
[58] P. Kabasakalian, unpublished data.

Analogously, 1-butyl nitrite (70) failed[46] to give dimeric 1-nitrosopropane, the expected product of a decomposition reaction, although a modest yield of dimeric 1-nitroso-4-butanol (71) resulted via the Barton reaction.

$$\underset{70}{CH_3(CH_2)_3CH_2ONO} \rightarrow \underset{71}{(CH_2NO(CH_2)_3CH_2OH)_2}$$

The only primary alkoxy radical which has so far been shown to undergo C—C fission (see however, Section IIIB-5 on nitrites *bearing an oxygen function on the α-carbon* atom) is that derived from 2-phenyl 1-ethyl nitrite[26] (72). Photolysis of 72 in benzene gave ω-nitrosotoluene dimer (75) and formaldehyde in accord with the mechanism shown:

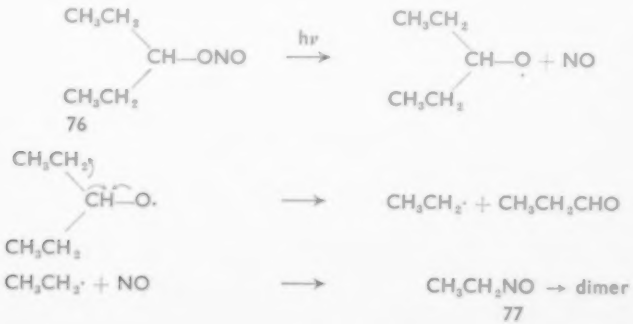


In this instance, then, the alkoxy radical (73) can suffer C—C fission to give the resonance-stabilized benzyl radical (74).

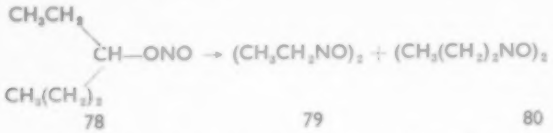
2. *Secondary alkoxy radical decomposition*

A large group of secondary alkyl nitrites has been investigated recently[46] and the salient results will be summarized here.

In the case of 2-propyl nitrite,[46] where methyl radicals are the only possible result of C—C fission, no nitrosodimer was observed. However, 3-pentyl nitrite (76) which can decompose to give *ethyl* radicals gave (albeit in low yield) dimeric nitrosoethane (77):

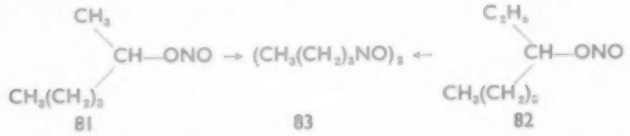


3-Hexyl nitrite[46] (78) can give rise to *ethyl or propyl* radicals by the carbon-carbon fission reaction. In fact, *both* 1-nitrosopropane dimer (80) and 1-nitrosoethane dimer dimer (79) were formed (as well as 1-nitroso-4-hexanol dimer, the intramolecular hydrogen abstraction product).



78 79 80

The point is further illustrated by 2-hexyl nitrite[46] (81) and 3-heptyl nitrite[46] (82) both of which gave only 1-nitroso butane dimer (83) by the C—C fission reaction (as well as good yields of the intramolecular hydrogen abstraction products).



81 83 82

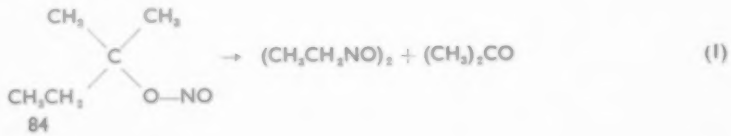
These examples, then, suggest that in C—C fission reactions of secondary nitrites, cleavage leading to the larger of two radicals is generally more likely.

In addition, the last two examples show that the Barton reaction involving intramolecular hydrogen abstraction at a secondary carbon atom is favored over the C—C fission reaction. This generalization is supported[46] by the observation that 5-nonyl nitrite, which has two available secondary carbon atoms for intramolecular hydrogen abstraction, gave no evidence for products of C—C fission.

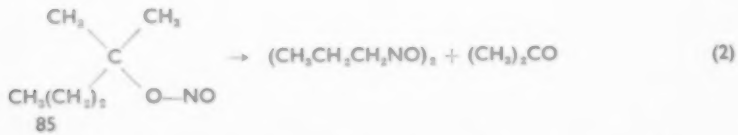
3. *Tertiary alkoxy radical decomposition*

In contrast to the results obtained by vapor phase photolysis (*cf.* section entitled Early Work), t-butyl nitrite in solution[46] failed to produce nitrosomethane dimer. However, the formation of acetone testified to the expected C—C cleavage reaction, and hence to the formation of methyl radicals.

Interestingly, 2-methyl-2-butyl and 2-methyl-2-pentyl nitrites[46] (84 and 85 respectively) furnished nitrosoethane dimer and 1-nitrosopropane dimer respectively in good yield (equations 1 and 2).



84 (1)



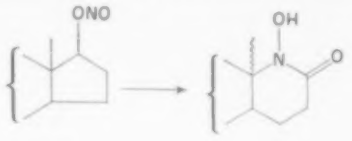
85 (2)

In the case of 2-methyl-2-pentyl nitrite[46] (85) the results indicated that decomposition of a tertiary alkoxy radical by C—C fission is favored over intramolecular hydrogen abstraction from a *primary* carbon atom. However, when intramolecular

hydrogen abstraction from a secondary or tertiary carbon is possible, no C—C fission is observed (see Section I).

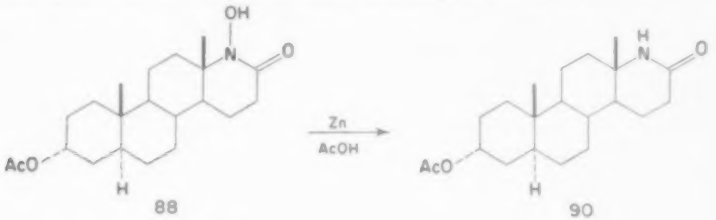
4. C—C *Fission reactions of alicyclic alkoxy radicals*

An example of ring fission suffered by an alicyclic alkoxy radical has recently been observed[59] in the steroid series through photolysis of steroidal 17-nitrites, such as 86, which resulted in the corresponding hydroxamic acids (part structure 87).

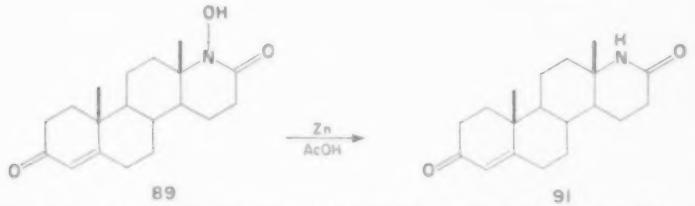


86 87

Structure-proof for the specific products 88 and 89 was obtained by reduction (zinc–acetic acid) to the lactams 90 and 91 respectively. The constitution of the lactam (91) is well established[60] and authentic lactam (90) was prepared in these laboratories by Beckmann rearrangement of the appropriate 17-oxime.

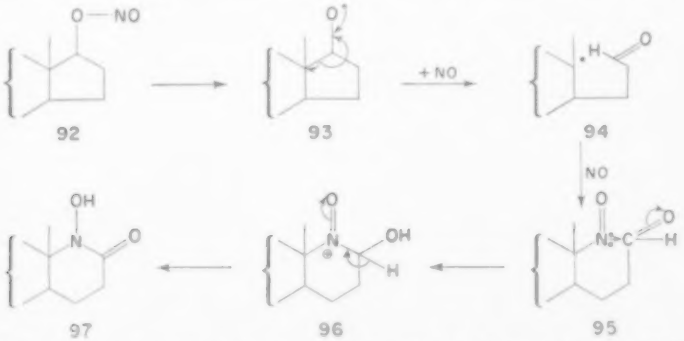


88 90



89 91

The formation of the hydroxamic acids can be rationalized in the following way (92 → 97):



92 93 94 95 96 97

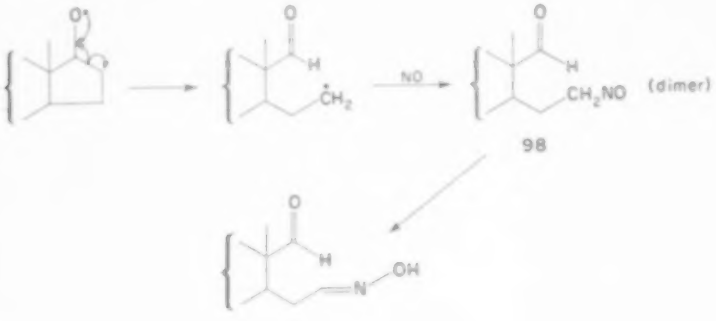
[59] C. H. Robinson, O. Gnoj, A. Mitchell, R. Wayne, E. Townley, P. Kabasakalian, E. P. Oliveto and D. H. R. Barton, *J. Amer. Chem. Soc.* **83**, 1771 (1961).

[60] B. M. Regan and F. N. Hayes, *J. Amer. Chem. Soc.* **78**, 639 (1956). One of us (C. H. R.) wishes to thank Dr. Regan for an authentic specimen of compound 91.

The alkoxy radical (93) undergoes ring fission to give the tertiary radical (94) which combines with NO to give the tertiary nitroso-aldehyde (95). The steps 95 to 97 then constitute a plausible route from the nitrosoaldehyde (95) to the observed product 97.

Extension of the reaction to 17-nitrites of the 1,3,5(10)-estratriene series again led to the isolation of hydroxamic acids, the structures of which were secured by reduction to known[60] lactams. However, in addition, isomeric hydroxamic acids were also obtained from the reaction mixtures: these latter arise from isomerism at C-13, in accord with the proposed mechanism.[61]

The alternative decomposition pathway for a C—17 alkoxy radical, involving cleavage of the bond between C-16 and C-17, should lead to the nitroso aldehyde (98) and thence to the nitrosodimer or oxime (99):



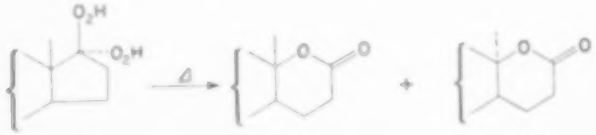
98

99

It has not been possible, however, to isolate such compounds from the photolyses of 17-nitrites. Presumably cleavage to give a tertiary radical is greatly favored relative to the formation of a primary radical.

However, recent work[46] with cyclopentyl nitrite (100) has shown that the dimeric

[61] The thermal decomposition of steroidal 17-bishydroperoxides has been investigated by Velluz and co-workers [*Bull. Soc. Chim. Fr.* 1484 (1952)] with the following results:

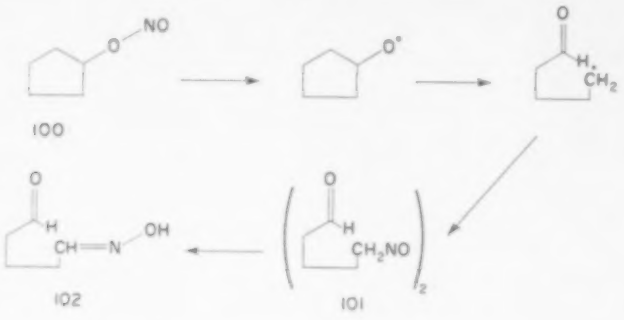


I II III

The decomposition of (I) most probably proceeds *via* the alkoxy radical (IV) which should cleave to the C-13 radical intermediate (V), subsequent ring closure giving rise to the epimeric lactones (II) and (III).

IV V

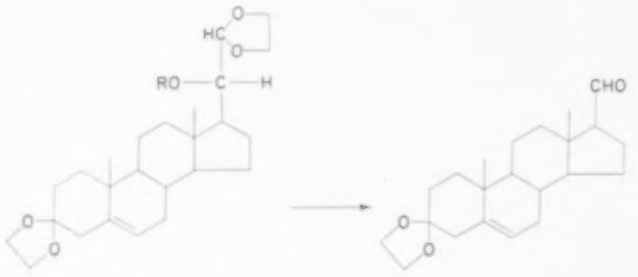
nitrosoaldehyde (101) is formed. The latter compound has been converted to the dialdehyde monoxime (102), characterized as the bis-oxime.



100 102 101

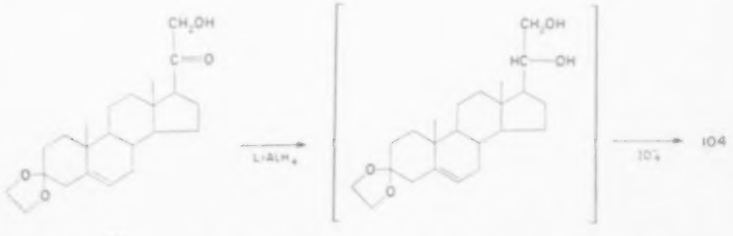
5. *Carbon–carbon fission in α-oxygenated nitrites*

An interesting series of degradative reactions has been observed in the steroid series.[62] In an attempt to extend the synthesis of 18-substituted substances related to aldosterone by the Barton reaction, the recently described 3,3:21,21-bis(ethylenedioxy)-5-pregnen-20β-ol (102, R = H)[63] was converted to its nitrite, and photolyzed.



103 104

The resulting material turned out to be the etio-aldehyde (104), as was proved by an independent synthesis (105[64] to 104).



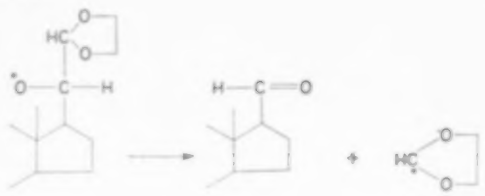
105

[62] A. L. Nussbaum, C. H. Robinson, E. P. Oliveto and D. H. R. Barton, in preparation. This work was stimulated by J. M. Beaton, who observed a transformation analogous to 103 to 104 in the 11-oxygenated series.

[63] K. Tsuda, N. Ikekawa and S. Nozoe, *Chem. Pharm. Bull. (Japan)* **7**, 519 (1959).

[64] R. Antonucci, S. Bernstein, R. Lenhard, N. J. Sax and J. H. Williams, *J. Org. Chem.* **17**, 1369 (1952).

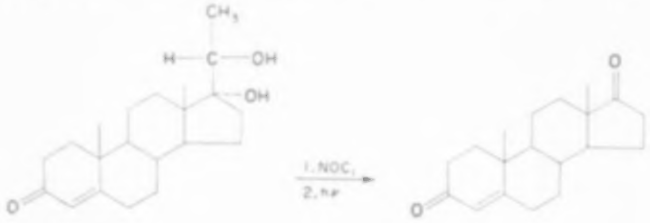
This carbon–carbon fission is very probably facilitated by the relative stability of the expelled fragment (106):



106

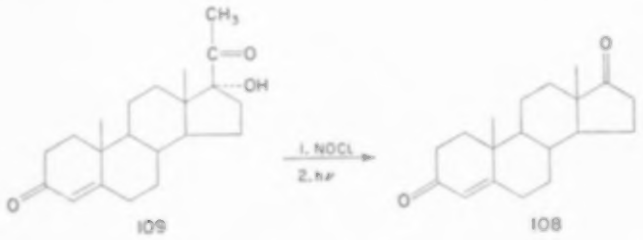
The question arose, what kind of substituents would favor such a fission reaction. A number of aliphatic 1,2-glycol dinitrites are known to suffer similar oxidative cleavage in pyrolytic experiments,[65] and a similar fate was expected by the photolytic method.

Indeed, the steroidal glycol 17α,20β-dihydroxy-Δ⁴-pregnen-3-one[66] (107) gave a nitrite which, upon irradiation, gave rise to Δ⁴-androstene-3,17-dione (108).

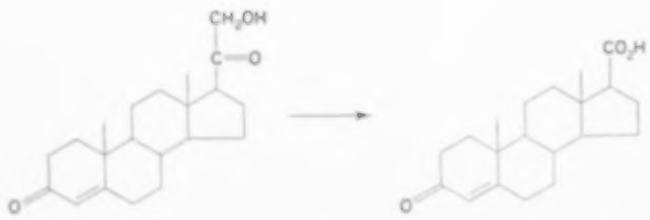


107 108

Two further examples involve α-hydroxyketones (109) and (110) which also underwent oxidative fission:



109 108



110

[65] L. P. Kuhn and L. DeAngelis, *J. Amer. Chem. Soc.* **76**, 328 (1954). See also J. Powling, quoted in ref. 15.
[66] J. Romo, M. Romero, C. Djerassi and G. Rosenkranz, *J. Amer. Chem. Soc.* **73**, 1528 (1951).

It would appear, then, that in the special case where a nitrite to be photolyzed is originally substituted by a certain type of oxygen-bearing moiety, an oxidative fission occurs during photolysis in competition with, and perhaps to the exclusion of, alternate modes of reaction. The full scope of this reaction is under investigation.

IV. ASSOCIATION WITH OTHER RADICALS

There is one instance in the course of recent work which would seem to bear out the concept of a photolytically generated alkoxy radical recombining directly with another fragment. Kabasakalian and Townley[44] observed that the photolysis of 1-octyl nitrite, in the presence of oxygen, results in a good yield of the corresponding nitrate. This may be rationalized by accepting the proposal of Hanst and Calvert:[67]

$$2NO + O_2 \rightarrow NO_2 \quad (1)$$

$$CH_3(CH_2)_6\ CH_2O\cdot + NO_2 \rightarrow CH_3(CH_2)_6CH_2ONO_2 \quad (2)$$

Alternately, the direct oxidation of light-activated nitrite may be considered:

$$CH_3(CH_2)_6CH_2ONO + h\nu \rightarrow CH_3(CH_2)_6CH_2ONO^* \quad (3)$$

$$2CH_3(CH_2)_6CH_2ONO^* + O_2 \rightarrow 2CH_3(CH_2)_6CH_2ONO_2 \quad (4)$$

Considering, however, the mechanism proposed for nitrate formation during nitrite pyrolysis in the presence of NO_2[68], the present reviewers consider (1) and (2) preferable.

CONCLUSION

Recent developments in the photochemistry of organic nitrites have shown that all data may be explained by the known reaction pathways of alkoxy radicals. A special feature is the overriding importance of intramolecular hydrogen abstraction (Barton Reaction) when photolyses are carried out in solution, and when a postulated six-membered transition complex can form. From the preparative point of view, nitrite photolysis opens the way to a variety of structures heretofore not easily accessible.

Acknowledgements—We wish to thank Professor D. H. R. Barton for his kind interest in this review. Thanks are also due to Drs. M. M. Pechet, J. M. Beaton and their colleagues at the Research Institute for Medicine and Chemistry, as well as Drs. Kabasakalian, Oliveto and Reimann of these Laboratories for permission to present their data, some prior to publication. We are also indebted to Drs. Topliss, Herzog, Meyer and Mr. Shapiro, also of these Laboratories, for their helpful criticism during the preparation of this paper.

[67] P. L. Hanst and J. G. Calvert, *J. Phys. Chem.* **63**, 2071 (1953).
[68] See ref. 15, pp. 246, 247 and references cited therein.

VOL
17
196

Tetrahedron, 1962, Vol. 17, pp. 61 to 68. Pergamon Press, Ltd. Printed in Northern Ireland

ADDITION, SUBSTITUTION, AND TELOMERIZATION REACTIONS OF OLEFINS IN THE PRESENCE OF METAL CARBONYLS OR COLLOIDAL IRON*

A. N. Nesmeyanov, R. Kh. Freidlina, E. C. Chukovskaya, R. G. Petrova and A. B. Belyavsky
Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, Moscow

(*Received* 17 *May* 1961)

There are about fifty reactions known to be catalysed by metal carbonyls,[1] those for olefins being mainly of three types such as carbonylation, hydrogenation and isomerization. They are essentially effected in the presence of carbon monoxide and metal carbonyls under 400 atm and up to 300°. Reactions that seem to be similar to those catalysed by metal carbonyls also proceed on the surface of the catalysing metal in the presence of carbon monoxide.[1]

We suggest now several new ways to apply metal carbonyls as catalysts. The reactions under study proved to be specific in running without carbon monoxide usually used to regenerate metal carbonyls.

We have found[2] silicon hydrides to react with olefins with small amounts of iron pentacarbonyl at 100–140° in two directions according to schemes I and II to form saturated or unsaturated silanes.

$$R'R''R'''SiH + CH_2{=}CHR \xrightarrow{Fe(Co)_5} \begin{cases} \rightarrow R'R''R'''SiCH_2CH_2R & \text{I} \\ \rightarrow R'R''R'''SiCH{=}CHR & \text{II} \end{cases}$$

with R′, R″, R‴ being chlorine or alkyl and R the alkyl or functional group.

Of special interest was the reaction proceeding along scheme II, no catalytic reactions of direct substitution due to the action of silicon hydrides on olefins having been formerly known. The effect of various factors on the percentage of products obtained following schemes I or II is not always clear. In some cases an excess of silicon hydride favours the formation of saturated compounds along scheme I and an excess of olefins that of unsaturated products via scheme II. See Table 1.

The direction of addition following scheme I was determined by structural study of the saturated addition product of methyldichlorosilane to propylene. The compounds were methylated with Grignard reagent, the products isolated were treated with conc sulphuric acid to dissolve unsaturated silanes and the saturated remainder was conventionally purified identified by its constants, analysis and Raman spectra as n-propyltrimethylsilane[2]. The direction of addition proved thus to be the same as when carrying the reaction in the presence of platinum or peroxides.

Instanced by the reaction of methyldichlorosilane and decene-1 the process was shown to be catalysed only by iron pentacarbonyl without any co-catalysts, unlike the reaction of methyldichlorosilane with acrylonitrile described below.[2] Indeed methyldichlorosilane and decene-1 react in the presence of iron pentacarbonyl

* Translated by A. L. Pumpiansky, Moscow.

[1] H. W. Sternberg, R. Markby and J. Wender *Chem. & Ind.* **42**, 41 (1960).

[2] R. Kh. Freidlina, E. C. Chukovskaya, J. Tsao and A. N. Nesmeyanov, *Dokl. Akad. Nauk. SSSR* **132**, 374 (1960).

TABLE 1. REACTION OF SILICON HYDRIDES AND OLEFINS IN THE PRESENCE OF IRON PENTACARBONYL OR COLLOIDAL IRON

N N	Silicon hydride	Olefin	Silicon hydride / Olefin (mole)	Structure of resulting products	Conversion of silan accounted for by the charget silan (%)	Overall yield of I and II	Relative yield (%)	
							I	II
				$Fe(CO)_5$				
1	$(C_2H_5)_3SiH$	$CH_2{=}CH_2$	3:1†	$(C_2H_5)_4Si$‡ I	100	79	100	—
2	$(C_2H_5)_3SiH$	$CH_2{=}CH_2$	1:5	$(C_2H_5)_3SiCH{=}CH_2$ II	73	92	—	100
3	CH_3SiCl_2H	$CH_2{=}CH_2$	1:7	$CH_3SiCl_2C_2H_5$ I	57	89	100	—
4	$SiCl_3H$	$CH_3CH{=}CH_2$	1:3	$Cl_3SiC_3H_7$ I $Cl_3SiC_3H_5$ II	34	85	50	50
5	$SiCl_3H$	$CH_3CH{=}CH_2$	2:1†	$Cl_3SiC_3H_7$ I $Cl_3SiC_3H_5$ II	48	83	60	40
6*	CH_3SiCl_2H	$CH_3CH{=}CH_2$	3:1†	$CH_3SiCl_2C_3H_7$ I $CH_3SiCl_2C_3H_5$ II	49	79	75	25
7*	CH_3SiCl_2H	$CH_3CH{=}CH_2$	1:4	$CH_3SiCl_2C_3H_7$ I $CH_3SiCl_2C_3H_5$ II	67	73	25	75
8*	CH_3SiCl_2H	$CH_3CH{=}CH_2$	1:8	$CH_3SiCl_2C_3H_7$ I $CH_3SiCl_2C_3H_5$ II	66	83	5	95
9	CH_3SiCl_2H	$C_5H_{11}CH{=}CH_2$	1,25:1	$CH_3SiCl_2C_{10}H_{21}$ I $CH_3SiCl_2C_{10}H_{19}$ II	39	94	20–30	70–80
10	CH_3SiCl_2H	$C_8H_{17}CH{=}CH_2$	5:1†	$CH_3SiCl_2C_{10}H_{21}$ I $CH_3SiCl_2C_{10}H_{19}$ II	39	91	20–30	70–80
11	$(C_2H_5)_3SiH$	$CH_2{=}CHOC_2H_5$	1:1,5	$(C_2H_5)_3SiOC_2H_5$ I $(C_2H_5)_3SiCH{=}CHOC_2H_5$ II	52	100	52·5	47·5
				Colloidal iron				
12	CH_3SiCl_2H	$CH_2{=}CH_2$	1:4	$C_2H_5SiCl_2CH_3$ I	44	90	100	—
13	CH_3SiCl_2H	$CH_3CH{=}CH_2$	1:3	$CH_3SiCl_2C_3H_7$ I $CH_3SiCl_2C_3H_6$ II	24	80	20	80

* These runs gave rise to a considerable amount of solid polypropylene.
† Conversion in these runs was estimated in percentage to 1 mole of silane charget.
‡ The reaction also led to 4 per cent yield of $(C_2H_5)_3SiCH_2CH_2Si(C_2H_5)_3$.

in nitrogen both in sealed glass ampoules and autoclave to form the same products in similar yields. This reaction allowed us to establish that during the formation of unsaturated silanes following scheme II it is decene that is acting as hydrogen acceptor to be thereby hydrated to n-decane.

The Raman spectra of the mixture of trimethyl derivatives obtained after methylation with Grignard reagent of the sum of products formed in the reaction between methyldichlorosilane and decene-1 revealed in the C=C range two bands, one at 1615 cm^{-1} and the other at 1662–1670 cm^{-1} split into two components. This allows to deduce that the mixture contained both a vinyl compound $(CH_3)_3SiCH{=}CHC_8H_{17}$ and allylic *cis-trans*-isomers $(CH_3)_3SiCH_2CH{=}CHC_7H_{15}$ (*cf.*[3,4,5]).

To elucidate the possibility of applying these reactions to unsaturated compounds involving reactive groups we have investigated the reaction of triethylsilane with vinylethyl ether and that of methyldichlorosilane and triethylsilane with acrylonitrile.[2,6,7] With vinylethyl ether the reaction yielded β-triethylsylylvinylethyl ether $(C_2H_5)_3SiCH{=}CHOC_2H_5$, whose structure was proved by acid hydrolysis to give acetaldehyde and hexaethyldisyloxane as well as by the absence in the infra-red spectrum 3000 and 3060 cm^{-1} of frequencies assigned to the terminal $=CH_2$ group.

The infra-red spectra in the C=C range revealed a double bond line, split into two components at 1597 and 1609 cm^{-1}, such a split being characteristic of vinyl ethers observed before.[8–10]

Ethoxytriethylsilane was also isolated. Its formation seems possibly to be due to β-decomposition of an intermediate saturated β-triethylsilyldiethyl ether $(C_2H_5)_3SiCH_2{-}CH_2OC_2H_5$ produced following scheme I.

It is to be particularly noted that in no instances mentioned above did a large excess of olefins or ethylene with its large excess up to the pressure of 500 atm give rise to telomer homologues.

Some of the described reactions when carried out in the presence of colloidal iron led to results similar to those obtained with iron pentacarbonyl. Thus, methyldichlorosilane and ethylene in the presence of colloidal iron gave methyldichlorosilane, and with propylene produced correspondingly a mixture of saturated and unsaturated silanes (see Table 1).

The investigation of the reaction of silicon hydrides and acrylonitrile gave different results. The reaction was carried out in a stainless steel autoclave or sealed glass ampoules at 120–150° with no catalyst or with iron pentacarbonyl, nickel chloride or their mixture. The results had been reported in detail[9] and can be summarized here as follows. In the absence of catalysts or in the presence of nickel chloride alone there is no reaction. Triethylsilane fails to react with acrylonitrile in the presence of iron pentacarbonyl or colloidal iron in an autoclave. Methyldichlorosilane does not react with acrylonitrile in the presence of iron pentacarbonyl in a sealed glass ampoule, but under the same experimental conditions in an autoclave an adduct is formed whose yield increases with increasing excess acrylonitrile. These data permitted to suggest

[3] A. D. Petrov, Yu. P. Yegorov, *et al. Izv. Akad. Nauk, SSSR, Otdel Khim. Nauk* 50 (1956).
[4] Yu. P. Yegorov, *Izv. Akad. Nauk. SSSR, Otdel Khim. Nauk.* 124 (1957).
[5] A. D. Petrov, S. I. Sadikh-Zade, *et al., Zh. Obsch Khim.* **24**, 2479 (1957).
[6] R. Kh. Freidlina, I. Tsao and E. C. Chukovskaya, *Dokl. Akad. Nauk SSSR* **132**, 149 (1960).
[7] R. Kh. Freidlina, E. C. Chukovskaya and I. Tsao *Dokl. Akad. Nauk SSSR* **127**, 352 (1959).
[8] M. I. Batuyev, E. N. Prilezhaeva and M. F. Shostakovsky, *Izv. Akad. Nauk Otdel. Khim. Nauk SSSR*, 123 (1947).
[9] A. Kirrmann, P. Chancel, *Bull. Soc. Chim. Fr.* 1388 (1954).
[10] P. P. Shorygin, T. N. Shkurina, *et al., Izv. Akad. Nauk SSSR, Otdel Chim. Nauk* In press.

that the reaction takes place because the mixture contains, in addition to iron carbonyl, traces of heavy metal salts formed on the autoclave walls under the action of chlorosilanes.

A similar effect of traces of heavy metal salts was observed when cyanoethylating silicochloroform in autoclaves in the presence of pyridine.[11] Indeed, when iron pentacarbonyl and nickel chloride are both present in small amounts acrylonitrile adds both methyldichlorosilane and triethylsilane. The reactions proceed equally

TABLE 2. REACTION OF $C_2H_5OCO(CH_2)_4SH$ WITH UNSATURATED COMPOUNDS

Unsaturated compound	Molar ratio mercaptan / unsat. comp.	Initiator	Temp(C°)	Time(hr)	Adduct yield (% of theory)
$CH_2{=}CHCO_2CH_3$	3	without initiator	175–200	7·5	20
$CH_2{=}CHCO_2CH_3$	3	$Fe(CO)_5$	130–150	4	85
$CH_2{=}CHCO_2CH_3$	3	Bz_2O_2	80–85	3·5	31*
$CH_2{=}CHCN$	4	without initiator	140–150	5	41
$CH_2{=}CHCN$	4	$Fe(CO)_5$	140–150	5	85
$CH_2{=}CHCN$	4	Bz_2O_2	80–85	3·5	76
$CH_2{=}CHCN$	4	colloidal iron	140–150	2·5	91

* Accounted for by the mercaptoester that had reacted. In addition to the adduct, such telomers as $C_2H_5OCO(CH_2)_4S(CH_2CHR)_nH$ were isolated, where $n = 2$ and 3, in 15·3 and 16·5 per cent yield, respectively.

well in an autoclave and in sealed ampoules, addition giving rise to α-methyldichlorosilylpropionitrile $CH_3SiCl_2CH(CH_3)CN$ with methyldichlorosilane or α-triethylsilylpropionitrile $(C_2H_5)_3SiCH(CH_3)CN$ with triethylsilane.

We have further found iron pentacarbonyl and colloidal iron to catalyse mercaptane addition to acryl compounds and succeeded in effecting reactions between ethyl δ-mercaptovalerate and acrylonitrile and methylacrylate (see Table 2). The reaction gave high yields at 130–150° following scheme III:

$$C_2H_5OCO(CH_2)_4SH + CH_2{=}CHR \rightarrow C_2H_5OCO(CH_2)_4SCH_2CH_2R$$

with R = CN, CO_2CH_3.

The reactions could also be effected without any catalyst but at higher temperatures and in substantially decreased yields (see Table 2). The reaction of mercaptane in the presence of iron carbonyl, even with a high excess of methylacrylate or acrylonitrile, does not lead to telomer homologues. In the presence of benzoyl peroxide, methylacrylate is telomerized by ethyl δ-mercaptovalerate to form a mixture of telomer homologues

$$C_2H_5OCO(CH_2)_4S[(CH_2)CH]_nH, \quad \text{with } CO_2CH_3$$

from which were isolated compounds with $n = 1, 2, 3$.

With acrylonitrile, and in the presence of benzoyl peroxide only, a corresponding adduct was formed. Those obtained using iron pentacarbonyl, colloidal iron, benzoyl peroxide, or by heating in the absence of catalysts proved to be identical and appeared to have the structure $C_2H_5OCO(CH_2)_4SCH_2CH_2R$ with R being CO_2CH_3, CN.

[11] S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Japan* **29**, 323, 326 (1956).

VOL. 17 1962

Considering the fact that in the presence of iron pentacarbonyl it is possible to add smoothly to olefins and their derivatives various compounds containing a labile hydrogen-element bond, and that these reactions are not affected by telomerization, it was thought of interest to study the reaction of ethylene and chloroform as well as other chloromethanes in the presence of metal carbonyls. Iron pentacarbonyl, as well as chromium, molybdenum, and tungsten hexacarbonyls were found to initiate the ethylene telomerization reaction by chloroform or carbon tetrachloride*[12,13] and iron pentacarbonyl by ethyltrichloroacetate. The most useful metal carbonyls investigated proved to be iron pentacarbonyl and chromium hexacarbonyl whose presence allowed us to obtain at 100–130° the same products as with benzoyl peroxide. A close similarity was observed in the extent of conversion of polychloromethanes and the yields of telomer homologues, under comparable conditions, but using as a catalyst iron pentacarbonyl or benzoyl peroxide.

Molybdenum and tungsten hexacarbonyls proved, under much the same conditions, less effective not only due to a lower conversion but also the formation of a complex mixture of by-products when ethylene was telomerized by chloroform or carbon tetrachloride (see Table 3).

There are not yet enough data to judge on the mechanism of the reactions under study. It seems, however, rather difficult to envisage them as proceeding along a single mechanism.

The reactions under discussion can be divided into two classes. The first class involves silicon hydride and mercaptan additions to unsaturated compounds and telomerization of ethylene by polychloromethane. Iron pentacarbonyl or colloidal iron may be supposed to form with unsaturated compounds π-complexes that actually catalyse these reactions. The second class comprises the addition of silicon hydrides to acrylo nitrile in the presence of iron pentacarbonyl and nickel chloride.

It is to be noted that the conditions leading to optimum conversion in the reactions in question were not studies. Therefore we did not deem it possible to discuss the relationship between the structure of starting compounds and the extent of the conversion observed.

EXPERIMENTAL

1. *The reaction of triethylsilane and ethylene*

The reaction was carried out with excess ethylene to obtain triethylvinylsilane. A stainless steel (500 cm) autoclave was charged with $(C_2H_5)_3SiH$ (34 g) and $Fe(CO)_5$ (0·5 ml). The air was substituted by nitrogen and ethylene fed up to 45 atm. After heating for 5 hr at 130° pressure was allowed to drop from 70 to 35 atm. Overall yield: 39·5 g with 27 g of triethylvinylsilane isolated. After repeated distillation: b.p. 144·5°; n_D^{20} 1·4330; d_4^{20} 0·7718 (Found: Mr, 47·92. Calc. for $C_8H_{18}Si$†, 48·26), lit.[16] (Found: C, 67·27, 67·39; H, 12·96, 13·18. $C_8H_{18}Si$ requires C, 67·57; H, 12·75%).

Raman spectrum‡ is in agreement with that reported for triethylvinyl silane.[18] The product was

* Shortly after the publication of our paper[12] we got to know that a British Patent[14] also mentioned the possibility of using iron pentacarbonyl and iron to initiate the telomerization of ethylene by CCl_4 and $CHCl_3$.

† The calculation here and further on was made using increments of groups suggested by Mirinov and Nikishin[19].

‡ Spectra referred to in this paper were all taken and interpreted by L. A. Leites (Institute of Chemistry of the U.S.S.R. Academy of Sciences).

[12] R. Kh. Freidlina and A. B. Belyavsky, *Dokl. Akad. Nauk SSSR* **127**, 1027 (1959).
[13] R. Kh. Freidlina and A. B. Belyavsky, *Izv. Akad. Nauk SSSR, Otdel Khim. Nauk* 177 (1961).
[14] Brit. Pat. 803,463; *Chem. Abstr.* 11222c (1959).
[16] K. A. Andrianov, *Organo-Silicon Compounds* p. 113. Moscow (1955).
[17] K. A. Andrianov, *Organo-Silicon Compounds* p. 414. Moscow (1955).
[18] Yu. P. Yegorov and P. A. Bazhulin, *Dokl. Akad. Nauk SSSR* **88**, 647 (1953).
[19] V. F. Mironov and G. I. Nikishin, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1080 (1958).

completely soluble in conc H_2SO_4, on dilution only hexaethyldisiloxane was isolated, b.p. 233°, n_D^{20} 1·4328; d_4^{20} 0·8448.

(Found: Mr, 75·85. Calc. for $C_{12}H_{30}Si_2O$ 76·08), lit.[17]

Repeating the experiment under initial ethylene pressure of 5 atm with a pressure drop in the course of the reaction from 20 to 10 atm at 130° gave $(C_2H_5)_4Si$ in 73% yield (theory), accounted for by the triethyl silane that had reacted and hexaethyldisilylethane in 4% yield.

2. *The reaction of propylene and methyldichlorosilane*

(a) *In the presence of iron pentacarbonyl.* A stainless steel autoclave (500 cm³) was charged with 57 g of CH_3SiCl_2H (0·5 mole), 1 ml of $Fe(CO)_5$ and 108 g of C_3H_6 (2·5 moles). It was heated at 130–140° for 4 hr. Overall yield: 70 g. After separation of unreacted CH_3SiCl_2H, 42 g of a fraction, b.p. 124–127°, n_D^{20} 1·4395, d_4^{20} 1·0593, were produced (*cf.* a similar experiment in ref. 2).

Methylation with Grignard reagent gave a fraction b.p. 85–87° n_D^{20} 1·4065, d_4^{20} 0·7186.

Below are given comparative literature data for trimethylalkenylsilanes and trimethylpropyl silane[16,20]

	b.p.	n_D^{20}	d_4^{20}
$(CH_3)_3SiCH{=}CHCH_3$	86–87°	1·4086	0·7167
$(CH_3)_3SiCH_2CH{=}CH_2$	84·9	1·4074	0·7193
$(CH_3)_3Si{-}C(=CH_2){-}CH_3$	82·8–83	1·4070	0·7186
$(CH_3)_3SiC_3H_7$-*n*	90°	1·3918	0·7020

The Raman spectra substantiated that the product obtained was indeed mostly $(CH_3)_3SiCH{=}CHCH_3$. 1 ml of this fraction was treated with 4 ml of conc H_2SO_4 resulting in a violent reaction accompanied by strong heating and dissolution of the whole product to leave a minute organic layer —0·08 mm thick.

(b) *In the presence of colloidal iron.* The experiment was conducted as above. An autoclave was charged with 119 g (1·05 moles) of CH_3SiCl_2H, 132 g of C_3H_6 (3 moles) and 2 ml of colloidal iron solution prepared as reported[21] to yield 30 g of a fraction, b.p. 115–130° (boiling mainly at 124–127°), n_D^{20} 1·4370, d_4^{20} 1·0537. Methylation with Grignard reagent led to a substance, b.p. 86–87·5°, n_D^{20} 1·4050, d_4^{20} 0·7181. (Found: C, 62·25, 62·31; H, 12·97, 13·17. $C_6H_{14}Si$ requires: C, 63·08; H, 12·35; Si, 24·57. $C_6H_{16}Si$ requires: C, 61·98; H, 13·87; Si, 24·15%).

On treatment of 1 ml of the substance with 4 ml of conc H_2SO_4 0·8 ml of the substance dissolved to leave 0·2 ml of undissolved organic layer.

Raman spectra revealed bands assigned to $(CH_3)_3SiCH{=}CHCH_3$ and $(CH_3)_3SiC_3H_7$—n.

3. *Cyanoethylation of silicon hydrides*

(a) *Reaction with methyldichlorosilane.* A stainless steel autoclave was charged with 115 g (1 mole) of CH_3SiCl_2H, 160 g (3 moles) of $CH_2{=}CHCN$, 1 ml of $Fe(CO)_5$ and 0·15 g of $NiCl_2$. The air was substituted by nitrogen and then nitrogen was fed up to 30 atm. After heating for 5 hr at 120–130° the reaction mixture was fractionated *in vacuo* to give 120 g (72% of theory). of α-methyldichlorosilyl-propionitrile, b.p. 59–60°/1 mm, n_D^{25} 1·4490, d_4^{20} 1·1635. (Found: Mr, 38·74. Calc. for $C_4H_7SiCl_2N$: 38·62). (Found: Si, 17·21, 16·88. Calc.: Si, 16·71%). Titration of 0·1 N NaOH gave: Cl, 42·49, 42·41. $C_4H_7SiCl_2N$ requires: Cl, 43·17%).

The structure of the adduct was proved as usual.[9,11] α-Methyldichlorosilyl propionotrile was methylated with methylmagnesiumiodide to give α-trimethyl silyl propionitrile. Yield 80%, b.p. 71·5°/20 mm, n_D^{20} 1·4245, d_4^{20} 0·8303. (Found: Mr, 39·14. Calc. for $C_6H_{13}SiN$: 39·09), lit.[11]: n_D^{25} 1·4232, d_4^{25} 0·8254. (Found: C, 56·64, 56·55; H, 10·47, 10·37; Si, 22·08, 22·39. $C_6H_{13}SiN$ requires: C, 56·63; H, 10·30; Si, 22·05%).

[20] A. D. Petrov and G. I. Nikishin, *Zh. Obschei Khim.* **26**, 1233 (1956).
[21] C. I. Sims and E. W. S. Mardles, *Trans. Faraday Soc.* **22**, 364 (1926).

VOL. 17 1962

TABLE 3

Run	Carbonyl	Telogen	Amount of telogen (g)	Pressure change at 115–120°	Telogen conversion (%)	Telomer homologues obtained (g): $CCl_3(CH_2CH_2)_nX$ (X = H,Cl)* or $Cl(CH_2CH_2)_nCCl_2CO_2C_2H_5$				
						$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n > 4$
1	$Cr(CO)_6$	$CHCl_3$	223	110–75	27	(7)	20	12	5	(22)
2	$Cr(CO)_6$	CCl_4	240	100–60	52	(20)	84	30	10	(15)
3	$Cr(CO)_6$	CCl_4	240	35–5	—	33	(18)			
4	$Mo(CO)_6$	CCl_4	240	115–80	23		13		(6)	
5	$W(CO)_6$	CCl_4	240	110–95	20	(8)	27	7		
6	$Fe(CO)_5$	CCl_4	236	130–100†	70	(8)	53	36	11	(23)
7	$Fe(CO)_5$	$HCCl_3$	440	230–140‡	41	(17)	32	21	15	(56)
8	$Fe(CO)_5$	$CCl_3CO_2C_2H_5$	125		72	34	42	6	(63)§	

* Figures not included in brackets indicate the weight of individual compounds produced. Those in brackets denote the weight of the product obtained as a broad fraction.

† At reaction temperature 100–105°.

‡ At reaction temperature 130–135°.

§ The weight of the fraction $n > 3$.

(b) *Reaction with triethylsilane.* The experiment was conducted as with methyldichlorosilane. 87 g (0·73 mole) of triethylsilane, 132 g (2·5 moles) of acrylonitrile, 0·5 ml of $Fe(CO)_5$ and 0·2 g of $NiCl_2$ yielded 92 g (73% of theory) of a substance, b.p. 97–98°/8 mm. Repeated distillation resulted in n_D^{20} 1·4535, d_4^{20} 0·8534. (Found: Mr, 52·95. Calc. for $C_5H_{11}SiN$: 52·88). (Found: C, 63·77, 63·49; H, 11·38, 11·33; Si, 16·83, 16·85. $C_5H_{11}SiN$ requires: C, 63·85; H, 11·31; Si, 16·57%).

The infra-red spectrum of this compound reveals a band 2205 ± 10 cm^{-1} assigned to α-nitriles.

4. *Reaction of ethyl δ-mercaptovalerate with acrylonitrile*

(a) *In the presence of iron pentacarbonyl.* A mixture of ethyl mercaptovalerate (20 g, 0·12 mole), acrylonitrile (25 g, 0·47 mole) and iron pentacarbonyl (0·3 ml) was heated for 5 hr, in an autoclave after substitution of nitrogen for air at 140–150°.

The polymeric precipitate of acrylonitrile was filtered off and washed with chloroform, the filtrate and chloroform extract were poured together, the solvent separated and the residue distilled *in vacuo*. Yield of addition product: 22·6 g (85% of theory), b.p. 158–160/3 mm, n_D^{20} 1·4790, d_4^{20} 1·0599. (Found: Mr, 57·52. Calc. for $C_{10}H_{17}O_2SN$: 57·73). (Found: C, 55·66, 55·59; H, 7·95, 8·00; S, 14·33, 14·28. Calc.: C, 55·81; H, 7·90; S, 14·88%).

The sulphide produced was saponified with alkali to 4-carboxybutyl-2-carboxyethyl sulphide, m.p. 78·5–79°. (Found: C, 46·29, 46·22; H, 6·76, 6·78; S, 15·67; 15·75. $C_8H_{14}O_4S$ requires: C, 46·60; H, 6·79; S, 15·53%). The mixed melting point with the sample produced on hydrolysis of 4-carbetoxybutyl-2-carbometoxyethyl sulphide showed no depression.

(b) *In the presence of colloidal iron.* The experiment was conducted as above.

Twenty grammes (0·12 mole) of mercaptoester and 25 g (0·47 mole) of acrylonitrile and colloidal iron produced from 1 ml of iron pentacarbonyl yielded 24·5 g (91% of theory) of pure adduct. Its hydrolysis led to 4-carboxybutyl-2-catboxyethyl sulphide, m.p. 78–79° whose mixed melting point with the sample obtained as in the previous experiment showed no depression.

5. *Reaction of ethyl δ-mercaptovalerate with methylacrylate in the presence of iron pentacarbonyl*

The experiment was conducted as above.

Ethyl δ-mercaptovalerate (15·5 g, 0·09 mole) methylacrylate (26·3 g, 0·3 mole) and iron pentacarbonyl (0·3 ml) were charged in an autoclave and after substitution of nitrogen for air heated at 130–150° for 4 hr. Distillation of the reaction mass over the column gave 4-carbethoxybutyl-2-carbomethoxyethylsulphide. Yield: 20·1 g (85% of theory), b.p. 146°/1 mm, n_D^{20} 1·4708, d_4^{20} 1·0803. (Found: Mr, 64·14. Calc. for $C_{11}H_{20}O_4S$: 64·30). (Found: C, 53·10, 52·92; H, 8·29, 8·15; S, 13·32, 13·16. Calc.: C, 53·22; H, 8·06; S, 12·90%).

Eight grammes of the sulphide were saponified to yield 5·7 g (85% of theory) of 4-carboxybutyl-2-carboxyethylsulphide, m.p. 78–79° (from water). The mixed melting point with samples from the previous experiments and those obtained by hydrolysing products produced thermally and in the presence of benzoyl peroxide showed no depression.

6. *Telomerization of ethylene in the presence of metal carbonyls*

The experiments were conducted in a rocking stainless steel autoclave (500 ml) charged with carbon tetrachloride, chloroform or ethyltrichloroacetate, the respective metal hexacarbonyl (0·1 g) or iron pentacarbonyl (0·5 ml). The air was substituted by nitrogen and ethylene introduced. The reaction mixture was heated for 4–5 hr at 100–130° and the products fractionated *in vacuo*, the results being listed in Table 3.

[22] A. D. Petrov and M. V. Vdovin, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1490 (1957).

Tetrahedron, 1962, Vol. 17, pp. 69 to 77. Pergamon Press, Ltd. Printed in Northern Ireland

VOL. 17 1962

SYNTHESIS OF α-CHLOROCARBOXYLIC ACIDS BY CHLORINATING COMPOUNDS CONTAINING THE CCl_2=CH GROUP IN ACID MEDIUM*

A. N. Nesmeyanov, R. Kh. Freidlina, V. N. Kost, T. T. Vassilyeva and B. V. Kopylova

Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, Moscow

(*Received* 9 *June* 1961)

The ready availability of α,α,α,ω-tetrachloroalkanes by telomerization of ethylene and carbon tetrachloride, their ability to react with nucleophilic, electrophilic and radical reagents made it possible for us to create on their basis a wide system of syntheses of bifunctional compounds.[1]

This paper reports on the results of our study to develop a method of synthesizing various tri- and poly-functional compounds according to the general scheme I.

$$\text{I.}\quad Cl(CH_2)_nCH_2CCl_3 \begin{cases} \xrightarrow{a} X(CH_2)_nCH_2CCl_3 \\ \xrightarrow{a'} Cl(CH_2)_nCH{=}CCl_2 \end{cases} \xrightarrow{b}$$

$$\longrightarrow X(CH_2)_nCH{=}CCl_2 \xrightarrow{c} X(CH_2)_nCHClCO_2H \longrightarrow X(CH_2)_nCHYCO_2H,$$

where X and Y are substituents, and n odd numbers† from 1 to 15.

This system is new in that it involves a one stage conversion of dichlorovinyl compounds to α-chlorocarboxylic acids (stage c), first instances of syntheses following this scheme having been reported in the paper mentioned above (see ref. 1).

To synthesize α-chlorocarboxylic acids we have worked out "conjugated addition" of chlorine to compounds containing the CCl_2=CH group in acid medium according to scheme II.

$$\text{II.}\quad X(CH_2)_nCH{=}CCl_2 \xrightarrow[HOAc]{Cl_2} [X(CH_2)_nCHClCCl_2OAc] \xrightarrow{H_2O}$$

$$\longrightarrow X(CH_2)_nCHClCO_2H + HCl$$

with Ac being the remainder of any acid.

Conjugated addition of various addenda to unsaturated hydrocarbons in different media has been known for a long time and is being extensively investigated. It has recently been suggested that conjugated addition of halogens to olefines proceeds through intermediate π-complexes of different types.[2-4]

* Translated by A. L. Pumpiansky, Moscow.

† n being limited to odd numbers is essential only when dichlorovinyl compounds are synthesized directly from α,α,α,ω-tetrachloroalkanes. Other routes to these compounds are, however, known that do not involve this restriction.

[1] A. N. Nesmeyanov, R. Kh. Freidlina and L. I. Zakharkin, *Quart. Rev.* **10**, 330 (1956).
[2] M. Dewar, *J. Chem. Soc.* 406, 777 (1946).
[3] E. A. Shilov, *Soobschenya Vses. Khim. Obsch. imeni Mendeleyeva*, **2**, 36 (1947).
[4] A. I. Titov and F. L. Maklyayev, *Zh. Obsch. Khim.* **24**, 1624 (1954).

Titov *et al.*[5] have found conjugated addition of halogen to the double bond of the CH_2=CH group in strong acid media such as sulphuric, phosphoric and arylsulphonic acids, to form corresponding β-haloalkyl esters. Nothing was, however, known of conjugated addition of halogens to the dichlorovinyl group.

Conjugated addition of chlorine to $RCH{=}CCl_2$ in different acids was carried out at 10–30°. Under these conditions almost no hydrolysis of starting compounds to corresponding acids RCH_2CO_2H was to be observed even in concentrated sulphuric acid. Usually chlorine saturation was continued until no hydrogen chloride was evolved, the mixture was diluted with water and extracted with chloroform. Acid

TABLE 1. CHLORINATION OF CCl_2=$CH(CH_2)_2Cl$ IN DIFFERENT MEDIA

Medium	Yield $Cl(CH_2)_3CHClCO_2H$ (% of theory)	Yield $Cl(CH_2)_3CHClCCl_3$ (% of theory)	Refs.
HCl*	—	81	7
$HClO_4$ (70%)	36	Neutral products were not investigated	7
CH_3CO_2H—$Hg(OAc)_2$†	62	36	8
HCOOH (anhydrous)	69	23	9
H_2SO_4 (93%)	78	8	6

* Trichloropentene in a mixture of ether and hydrochloric acid was simultaneously saturated with chlorine and hydrogen chloride.

† Mercuric acetate and trichloropentene were taken in equimolecular amounts.

products were isolated from chloroform with concentrated soda solution. By acidifying alkaline extracts acid reaction products were obtained. Fractionation of the residue after evaporation of chloroform gave rise to neutral products. In Tables 1–6 all yields are based on pure compounds. As a rule, all acids produced are characterized by their chloro anhydrides, anilides or other crystalline derivatives.

Taking 1,1,5-trichloropentene-1 as an example we have studied chlorination in different acid media (see Table 1).

It will be seen from the table that in all cases the two main reactions, that of conjugated addition, that is the introduction of the molecules from the medium, and that of usual chlorination of the double bond proceed concurrently. The latter reaction seems to be favoured by the appearance in the reaction mixture of hydrogen chloride. For the successful production of α-chlorocarboxylic acids it is therefore necessary to carry out the reaction under such conditions when hydrogen chloride is being bound (e.g. by adding mercuric acetate) or driven out of the medium (in anhydrous acids).

Chlorination in concentrated sulphuric acid can be recommended in all cases when starting compounds contain substituents that are not affected by this medium. (See Table 2). But when substituents are not inert to the action of sulphuric acid it is

[5] A. I. Titov and F. L. Maklyayev, *Zh. Obsch. Khim.* **24**, 1631 (1954).
[6] A. N. Nesmeyanov, V. N. Kost and R. Kh. Freidlina, *Dokl. Akad. Nauk SSSR* **103**, 1029 (1955).
[7] R. Kh. Freidlina, V. N. Kost and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1202 (1956).
[8] A. N. Nesmeyanov, V. N. Kost, T. T. Vassilyeva and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 152 (1958).
[9] V. N. Kost, T. T. Sidorova, R. Kh. Freidlina and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 2122 (1959).

better to synthesize α-chlorocarboxylic acids in acetic or formic acid. (See Tables 3 and 4). Thus in glacial acetic acid in the presence of mercuric acetate or in anhydrous formic acid we obtained corresponding α-chlorocarboxylic acids starting with compounds

$$R(CH_2)_nCH{=}CCl_2, \text{ where } R = C_6H_5,\ CH_3COO,\ HCOO,\ CH_3O,\ CN.$$

TABLE 2. CHLORINATION OF $RCH{=}CCl_2$ IN SULPHURIC ACID ($d = 1{\cdot}8$)

R	Yield $RCHClCO_2H$ (% of theory)	Refs.	R	Yield $RCHClCO_2H$ (% of theory)	Refs.
$CH_3(CH_2)_2$—	71	6	$HOOC(CH_2)_3$—	77	6
$CH_3(CH_2)_4$—	51	6	$HOOC(CH_2)_4$—	73	6
$ClCH_2$—	66	9	$HOOC(CH_2)_5$—	69	6
$Cl(CH_2)_2$—	78	6	$C_6H_4\begin{matrix}CO\\CO\end{matrix}N(CH_2)_3$—	92	11
$Cl(CH_2)_5$—	70	6	$C_6H_4\begin{matrix}CO\\CO\end{matrix}N(CH_2)_4$—	84	10
$CCl_3(CH_2)_2$—	52	7	p-$ClC_6H_4CH_2$—	83	12

TABLE 3. HALOGENATION OF $RCH{=}CCl_2$ IN GLACIAL ACETIC ACID IN THE PRESENCE OF MERCURIC ACETATE

R	Yield $RCHClCO_2H$ (% of theory)*	Yield $RCHClCCl_3$ (% of theory)	Refs.
CH_3OCH_2—	25	Neutral products were not investigated	8
CH_3COOCH_2—	27	55	8
$C_6H_5CH_2$—†	45 (54)	37	8
$Cl(CH_2)_3$—	62	30	8
$CH_3COO(CH_2)_3$—	55	35	8
$CN(CH_2)_3$—	54	30	8
$Cl(CH_2)_3$—‡	24 (48)	32	8

* Yields calculated for the product that had reacted are listed in parentheses.
† With no mercuric acetate the acid was obtained in 30% yield.[12]
‡ Bromine addition. $Cl(CH_2)_3CHBrCO_2H$ and $Cl(CH_2)_3CHBrCCl_2Br$ were produced.

We succeeded also in producing ω-chloro-α-bromopentanoic acid by making bromine react with 1,1,5-trichloropentene-1 in acetic acid in the presence of mercuric acetate.

[10] R. Kh. Freidlina, V. N. Kost, T. T. Vassilyeva and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 826 (1959).
[11] A. N. Nesmeyanov, R. Kh. Freidlina and R. G. Petrova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 451 (1957).
[12] R. Kh. Freidlina, N. A. Semenov and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 652 (1959).

VOL. 17 1962

In many instances, however, the yields of α-halo-carboxylic acids obtained in acetic acid still leave much to be desired. Curiously enough, bromination of fluoro-olefines containing the $>C{=}CF_2$ group in glacial acetic acid and in the presence of mercuric acetate or sulphate proceeds essentially with conjugated addition to form corresponding acetates of α,α-difluorosubstituted alcohols $CH_3CO_2CF_2\underset{|}{\overset{|}{C}}Br$.[13]

In anhydrous formic acid conjugated addition of chlorine to $CCl_2{=}CH$ gives rise to a high yield of α-chlorocarboxylic acids even with no mercuric acetate present. This synthetic alternative is rather convenient and applicable to many instances (see Table 4).

TABLE 4. CHLORINATION OF $RCH{=}CCl_2$ IN FORMIC ACID

R	Yield $RCHClCO_2H$ (% of theory)*	Yield $RCHClCCl_3$ (% of theory)	Refs.
CH_3OCH_2—	60	Neutral compounds were not investigated	10
$HCOOCH_2$—	73	16	10
$C_6H_5CH_2$—	63	29	9
$ClCH_2$—	52 (60)	31	10
$HCOO(CH_2)_3$—	82	9	10
$Cl(CH_2)_3$—	69	23	10
$Cl(CH_2)_5$—	76 (85)	9	10
$Cl(CH_2)_7$—	71 (82)	6	10
p-$C_6H_4(CH_2CH{=}CCl_2)_2$	30†	—	14

* Yields calculated for the product that had reacted are listed in parentheses.
† Dicarboxylic acid p-$C_6H_4(CH_2CHClCO_2H)_2$ was obtained.

With formic acid as reaction medium we succeeded in effecting the synthesis of almost not investigated α-chloro-ω-sulphocarboxylic acids by chlorinating isothiourea salts $HCl.NH_2(NH{=})CS(CH_2)_nCH{=}CCl_2$ according to scheme III.

$$\text{III. } HClNH_2(NH{=})CS(CH_2)_nCH{=}CCl_2 \xrightarrow[HCOOH]{Cl_2} \begin{cases} \longrightarrow HO_3S(CH_2)_nCHClCO_2H & (1) \\ \longrightarrow HO_3S(CH_2)_nCHClCCl_3 & (2) \end{cases}$$

Chlorination of alkylisothiourea hydrochlorides in aqueous medium is known to have been suggested as a method to obtain alkylsulphochlorides.[15,16,17] But the report[18] about the reaction mixture exploding when treated made limited its usefulness. Chlorinating in anhydrous formic acid without heating we observed no violent processes. Separation of acids (1) and (2) was based on the latter being less soluble in water. The former were isolated as their bis-benzylisothiouea salts, the latter as sodium salts. (See Table 5.)

[13] I. L. Knunyants, E. Ja. Pervova and V. V. Tuleneva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 843 (1956).
[14] A. N. Nesmeyanov, R. Kh. Freidlina and N. A. Semenov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1969 (1960).
[15] C. Ziegler and J. M. Sprague, *J. Org. Chem.* **16**, 621 (1951).
[16] J. M. Sprague and T. B. Johnson, *J. Amer. Chem. Soc.* **59**, 1837, 2439 (1937).
[17] T. B. Johnson and J. M. Sprague, *J. Amer. Chem. Soc.* **58**, 1348 (1936).
[18] K. Folkers, A. Russell and R. W. Bost, *J. Amer. Chem. Soc.* **63**, 3530 (1941).

It is to be noted that we were not concerned with optimum yields of α-chlorocarboxylic acids in all the instances under investigation. In a number of cases the yields might be probably increased. We did not deem it possible, therefore, to discuss the relationship existing between the structure of starting dichlorovinyl derivatives and the yield of corresponding reaction products.

The reactions under study showed that compounds containing $CCl_2{=}CH{-}$ with a relatively weak nucleophilic bond (that is a bond that does not seem to form readily π-complexes with halogens) can also undergo reactions of "conjugated addition" by a mechanism which has not yet been investigated and is of a special interest.

VOL. 17 1962

TABLE 5. CHLORINATION OF $HCl.NH_2(NH{=})CS(CH_2)_nCH{=}CCl_2$ IN FORMIC ACID

n	Yield of compound I* (% of theory)	Yield of compound II† (% of theory)
3	42·5	19
5	33.5	28·7
7	13–23	42
9	11–14·5	—

* Compound I is $HOOCCHCl(CH_2)_nSO_2H.2C_6H_5CH_2SC(=NH)NH_2$
† Compound II is $CCl_2CHCl(CH_2)_nSO_3Na.H_2O$.

As seen from instances given in Tables 1–5, α-chlorocarboxylic acids containing in ω-position different substituents can be readily obtained in high yield starting with compounds $X(CH_2)_nCH{=}CCl_2$. α-Chloroacids produced by this method are readily freed from by-products that consist of neutral substances or acids much less soluble in water. This makes this method superior to direct chlorination of carboxylic and dicarboxylic acids that often gives rise to a product mixture that is difficult to separate.

Many of the compounds obtained are useful as starting compounds for further synthesis.

Starting with a number of α-chlorocarboxylic acids produced by the above method we have, in particular, synthesized corresponding α-aminoacids including racemates of natural amino acids, as well as their analogues and homologs.

The available data on ammonolysis of α-halo carboxylic acids mostly refer to α-bromoderivatives whereas only isolated instances of α-chloroderivatives have been reported. This seems to be accounted for by the latter being less available and the difficulty to obtain them pure.

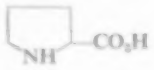
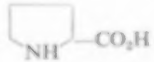
In some instances the yields of aminoacids are claimed to be substantially lower than using α-bromoderivatives.[19,20] This is likely to be due to chloroacids not being pure enough and the reaction conditions not well known. Our high yields of aminoacids on ammonolysis of α-chloroacids show that the yield of aminoacids seems to be little affected by the nature of the halogen in α-position. (See Table 6.)

Owing to the availability of starting compounds and high yields of products at all stages following scheme I this synthetic route to a number of α-amino acids must be considered superior to other methods known.

The method is illustrated below by representative syntheses of α-chloro acids under different conditions.

[19] R. Goudry, *Canad. J. Res.* **23 B**, 88 (1945).
[20] R. Goudry and L. Berlinguet, *Canad. J. Res.* **27 B**, 282 (1949).

TABLE 6. AMMONOLYSIS OF α-CHLOROCARBOXYLIC ACIDS WITH 25% AQUEOUS AMMONIA

Starting α-chloroacids	α-aminoacids	Yield (% of theory)	Refs.
$C_6H_5CH_2CHClCO_2H$	$C_6H_5CH_2CH(NH_2)CO_2H$*	77	9
p-$ClC_6H_4CH_2CHClCO_2H$	*p*-$ClC_6H_4CH_2CH(NH_2)CO_2H$*	70	9
$C_2H_5OCO(CH_2)_2CHClCO_2C_2H_5$	$HOOC(CH_2)_2CH(NH_2)CO_2H$†	70	9
$C_2H_5OCO(CH_2)_2CHClCO_2C_2H_5$	$HOOC(CH_2)_2CH(NH_2)CO_2H$‡	80	9
$HOOC(CH_2)_4CHClCO_2H$	$HOOC(CH_2)_4CH(NH_2)CO_2H$§	80	9
$HOOC(CH_2)_3CHClCO_2H$	$HOOC(CH_2)_3CH(NH_2)CO_2H$§	85	9
	$NH_2(CH_2)_4CH(NH_2)CO_2H.2HCl$	74	9
$Cl(CH_2)_3CHClCO_2H$		50	11 conf. (20)
	$NH_2(CH_2)_3CH(NH_2)CO_2H.HCl$	30	11
	+ 	21	
$CH_3OCH_2CHClCOOH$	$CH_3OCH_2CH(NH_2)COOH$	84	
$CH_3OCH_2CHClCOOH$	$HOCH_2CH(NH_2)COOH$	80	
$HCOOCH_2CHClCOOH$	$NH_2CH_2CH(OH)COOH$	83	

* Accompanied by dehydrochlorination of α-chloroacids.
† Ammonolysis with alcohol ammonia; glutamic acid and ammonium chloride separation is effected on cationite KU-2.
‡ Ammonolysis with alcohol ammonia.
§ Amino acid is purified from ammonium chloride with cationite KU-2.

VOL. 17 1962

EXPERIMENTAL

Chlorination of 1,1,5-*trichloropentene*-1 *in sulphuric acid*

Through a mixture of trichloropentene (90 g) and 93% sulphuric acid (130 g) chlorine was passed with stirring at 15–20° till no hydrogen chloride was evolved. After dilution with water the mixture was extracted with chloroform. Acid products were isolated from the chloroform layer, and washed with 10% sodium hydroxide solution. Acidification of alkaline extracts gave α,δ-dichlorovaleric acid, b.p. 106–107°/1 mm; n_D^{20} 1·4825; d_4^{20} 1·3421. (Found: MR, 36·37. Calc.: MR, 36·56). Yield of pure acid: 68 g (78% of theory). Lit.[21] for α,δ-dichlorovaleric acid: b.p. 129–131°/5 mm; n_D^{20} 1·4835; d_4^{20} 1·3421.

Acidechloride: b.p. 80°/5 mm; n_D^{20} 1·4840; d_4^{20} 1·3513 (Found: MR, 40·12. Calc. for $C_5H_7Cl_3O$: MR, 40·27).

Anilide: m.p. 58–59° (from petroleum ether plus benzene). (Found: C, 53·67, 53·69; H, 5·35, 5·50. $C_{11}H_{13}NCl_2O$ requires: C, 53·67; H, 5·32%).

In addition, 16·5 g of neutral products were obtained boiling at 60–75°/1 mm. Repeated distillation gave the starting trichloropentene (4 g) and 1,1,1,2,5-pentachloropentane (10 g), b.p. 86–87°/2 mm; n_D^{20} 1·5100; d_4^{20} 1·4806 (Found: MR, 49·39. Calc: MR, 49·62). Lit.[22] b.p. 121–122°/12 mm; n_D^{20} 1·5135; d_4^{20} 1·4807.

Chlorination of 1,1-*dichloro*-5-*cyanopentene*-1 *in acetic acid in the presence of mercuric acetate*

Through a mixture of dichlorocyanopentene (32·8 g), mercuric acetate (63·6 g), and glacial acetic acid chlorine was passed at 50° with stirring till its decoloration was no more observed. The precipitate was filtered off, acetic acid from the filtrate evaporated and the residue dissolved in ether with the mercuric salt precipitate filtered off. Acid products from ether solution were isolated with concentrated soda solution, the soda extracts acidified, repeatedly extracted with ether and dried over calcium chloride. Distillation gave 54% α-cloro-δ-cyanovaleric acid (17·4 g), b.p. 150° (1 mm), 162° (3 mm), n_D^{20} 1·4770, d_4^{20} 1·2660. (Found: MR, 36·06. Calc: MR, 36·13.) (Found: C, 44·47, 44·27; H, 5·09, 5·05; Cl, 22·24. $C_6H_8NClO_2$ requires: C, 44·60; H, 4·98; Cl, 21·95%. Acidechloride: b.p. 110° (2 mm); n_D^{20} 1·4830; d_4^{20} 1·3072 (Found: MR, 39·33. Calc.: MR, 39·47.[4]).

Sulphuric acid hydrolysis gave α-chloroadipinic acid, m.p. 102°. The melting point of the mixture with authentic α-chloroadipinic acid proved to be 102°.

In addition, 16·5 g of neutral products were obtained such as the starting 1,1-dichloro-5-cyanopentene (2·5 g), 1,1,1,2-tetrachloro-5-cyanopentane (14 g, 30%), b.p. 116° (2 mm); n_D^{20} 1·5045; d_4^{20} 1·4087. (Found: MR, 49·43. Calc.: MR, 49·19.) (Found: C, 31·09, 31·04; H, 3·03, 3·17. $C_6H_7NCl_4$ requires: C, 30·67; H, 3·00%).

Chlorination of 1,1-*dichloro*-3-*formoxypropene*-1 *in formic acid*

Through a mixture of 1,1-dichloro-3-formoxypropene-1 (40 g) and anhydrous formic acid (80 g) at 30° chlorine was slowly passed with stirring till no hydrogen chloride was evolved. After removal of formic acid and distillation *in vacuo*, α-chloro-β-formoxypropionic acid was obtained. Yield 29·6 g (73% of theory), m.p. 66–67° (from benzene). (Found: C, 31·68, 31·70; H, 3·34, 3·30. $C_4H_5ClO_4$ requires: C, 31·49; H, 3·34%).

In addition we obtained the starting formoxydichloropropene (2 g), 1,1,1,2-tetrachloro-3-formoxypropane (8·8 g, 18% of theory), b.p. 93–94° (7 mm); n_D^{20} 1·4932; d_4^{20} 1·5622 (Found: MR, 42·04. Calc.: MR, 41·79). (Found: C, 21·18, 21·30; H, 1·88, 1·92. $C_4H_4Cl_4O_2$ requires: C, 21·26; H, 1·78%).

Ammonolysis of α-chloro-β-formoxypropionic acid with 25% aqueous ammonia when heated at 70° for 10 hr in an autoclave gave isoserin. Yield 83% of theory, m.p. 239–240 (from water). Lit.[23] m.p. 237°. (Found: C, 34·02, 34·18; H, 6·93, 6·71; N, 13·20, 13·27. $C_3H_7NO_3$ requires: C, 34·29; H, 6·72; N, 13·32%).

Chlorination of $HCl.NH_2(NH{=})CS(CH_2)_2CH{=}CCl_2$ *in formic acid*

Through isothiourea chloride (5·5 g), produced from 1,1,5-trichloropentene-1, in anhydrous formic acid (25 ml) at 35° chlorine was slowly passed at the rate of about 50 ml/min till no hydrogen chlorine

[21] R. Kh. Freidlina and E. I. Vassilyeva, *Dokl. Akad. Nauk SSSR* **100**, 85 (1955).
[22] A. N. Nesmeyanov, R. Kh. Freidlina and L. I. Zakharkin, *Dokl. Akad. Nauk SSSR* **56**, 87 (1954).
[23] H. Rinderknecht and C. Niemann, *J. Amer. Chem. Soc.* **75**, 6322 (1953).

Table 7

Compound	m.p.(C°)	b.p.(C°)	n_D^{20}	d_4^{20}	Refs.
1. $ClCH_2CHClCOOH$	52–53	75/1·5			9
2. $ClCH_2CHClCCl_3$		110–111/30	1·5108	1·6121	9
3. $CH_3OCH_2CHClCOOH$*		79/1·5	1·4569	1·3216	8,9
Acidechloride*		63–65/24	1·4590	1·3216	8
4. $HCOOCH_2CHClCOOH$*	66–67	—	—	—	9
5. $HCOOCH_2CHClCCl_3$*		93–94/7	1·4932	1·5622	9
6. $CH_3COOCH_2CHClCOOH$*		112/1·5	1·4570	1·3496	8
Acidechloride*		90–91/17	1·4565	1·3671	8
7. $CH_3COOCH_2CHClCCl_3$		117–118/24	1·4860	1·4899	8
8. $C_6H_5CH_2CHClCOOH$*	51	132/2			8,10,12
Acidechloride*		74/2	1·5430	1·2647	8
amide	93	—	—	—	8
anilide*	125	—	—	—	8
ethyl ester*		110/8	1·5092	1·1312	8
9. $C_6H_5CH_2CHClCCl_3$		122/3	1·5555	1·3875	8
10. p-$ClC_6H_4CH_2CHClCOOH$	99·5	—	—	—	12
11. $C_2H_5OOCCHCl(CH_2)_2COOC_2H_5$*		93–94/1	1·4439	1·1388	10
12. $CH_3(CH_2)_2CHClCOOH$		93–94/5	1·4442	1·4445	6
Acidechloride*		61–62/28	1·4465	1·1765	6
anilide*	63–64	—	—	—	6
13. $Cl(CH_2)_3CHClCOOH$		107/1	1·4825	1·3421	6,7,8,9
Acidechloride*		80/5	1·4840	1·3513	6
anilide*	58–59	—	—	—	6
14. $Cl(CH_2)_3CHClCCl_3$		86–87/2	1·5100	1·4806	6,7
15. $HOOC(CH_2)_2CHClCOOH$	104–105				6
16. $CCl_3CH_2CH_2CHClCOOH$	82–83	—	—	—	7
17. $Cl(CH_2)_3CHBrCOOH$		106–107/0·5	1·5070	1·6215	8
18. $Cl(CH_2)_3CHBrCCl_2Br$		84–85/1	1·5562	1·9322	8
19. $HCOO(CH_2)_3CHClCOOH$*		138/1·5	1·4671	1·3148	9
20. $HCOO(CH_2)_3CHClCCl_3$*		101/2	1·4973	1·4503	9
21. $CH_3COO(CH_2)_3CHClCOOH$*		126–127/1	1·4640	1·2630	8
Acidechloride*		133/18	1·4668	1·2765	8
22. $CH_3COO(CH_2)_3CHClCCl_3$*		100–101/1·5	1·4870	1·3834	8
23. $NC(CH_2)_3CHClCOOH$*		150/1	1·4770	1·2660	8
Acidechloride*		110/2	1·4830	1·3072	8
24. $NC(CH_2)_3CHClCCl_3$*		116/2	1·5045	1·4087	8
25. $H_2N(CH_2)_3CHClCOOH$*	138	—	—	—	11
26. $C_6H_4(CO)_2N(CH_2)_3CHClCO_2H$	118–119				11
27. $C_6H_4(CO_2)N(CH_2)_4CHClCO_2H$	132	—	—	—	10
28. $CH_3(CH_2)_4CHClCOOH$*		92–93/1	1·4485	1·0830	6
Acidechloride		76–77/13	1·4498	1·1006	6
29. $Cl(CH_2)_5CHClCOOH$	22–24	128–131/1	1·4804	1·2441	6,9
Acidechloride*		104/2	1·4817	1·2557	6
anilide	42–43	—	—	—	6
30. $Cl(CH_2)_5CHClCCl_3$		102/2·5	1·5036	1·3715	9

TABLE 7 (*continued*)

Compound	m.p.(C°)	b.p.(C°)	n_D^{20}	d_4^{20}	Refs.
31. $HOOC(CH_2)_5CHClCOOH$	98–99	—	—	—	6
32. $Cl(CH_2)_7CHClCOOH$*		142–143/0·5	1·4768	1·1694	9
Acidechloride*		130/1	1·4785	1·1899	9
anilide*	62–63	—	—	—	9
33. $Cl(CH_2)_7CHClCCl_3$*		120–121/1·5	1·4980	1·2947	9
34. p-$C_6H_4(CH_2CHClCOOH)_2$	199–200	—	—	—	14
35. $HOOCCHCl(CH_2)_2SO_3H.$ $2C_6H_5CH_2SC(=NH)NH_2$	111–111·5				24
36. $HOOCCHCl(CH_2)_3SO_3H.$ $2C_6H_5CH_2SC(=NH)NH_2$	132–133				24
37. $HOOCCHCl(CH_2)_4SO_3H.$ $2C_6H_5CH_2SC(=NH)NH_2$	124–125				24
38. $HOOCCHCl(CH_2)_5SO_3H.$ $2C_6H_5CH_2SC(=NH)NH_2$	143				24

was evolved. Treatment of the reaction mixture with warm water resulted in the product of chlorine addition to the double bond obtained as oil with α-chlorocarboxylic acid remaining in the solution. The organic layer (1·5 g) was separated, treatment with concentrated soda solution gave sodium salt (CCl_3-$CHCl(CH_2)_3SO_3Na.H_2O$). Yield 1·35 g (19% of theory). (Found: C, 18·13, 17·95; H, 2·98, 2·76. $C_5H_9O_4Cl_4SNa$ requires: C, 18·18; H, 2·72%).

Evaporation of water layer *in vacuo* at 30–35° led to α-chlorocarboxylic acid (4·4 g). Treatment with aqueous soda and benzylthiourea chloride solution gave the salt of bis-benzylthiourea ($HOOCCHCl(CH_2)_3SO_3H.2C_6H_5CH_2SC(=NH)NH_2$). Yield 5·1 g (42·5% of theory), m.p. 111–111·5° (after three crystallizations from water). (Found: C, 45·63, 45·53; H, 5·35, 5·32. $C_{21}H_{29}O_3ClS_3N_4$ requires: C, 45·94; H, 5·29%).

In Table 7 are listed several constants of substances obtained by conjugated chlorination of compounds containing the dichlorovinyl group. Substances previously not reported are marked with an asterisk.

[24] R. Kh. Freidlina, B. V. Kopylova and A.N. Nesmeyanov. In press.

Tetrahedron, 1962, Vol. 17, pp. 79 to 87. Pergamon Press, Ltd. Printed in Northern Ireland

VOL.
17
1962

CHEMISTRY OF DINITROACETONITRILE—I

PREPARATION AND PROPERTIES OF DINITROACETONITRILE AND ITS SALTS[1]

CHARLES O. PARKER, WILLIAM D. EMMONS, HENRY A. ROLEWICZ and KEITH S. MCCALLUM
Rohm & Haas Co., Redstone Arsenal Research Division
Huntsville, Alabama

(*Received* 23 *March* 1961)

Abstract—Two general routes for the preparation of dinitroacetonitrile are known. One method[2] involving reduction of the intermediate trinitroacetonitrile has been modified and improved in both the preparative and degradative steps. Isolation of dinitroacetonitrile as its tetrahydrate, sodium, potassium, silver, ammonium, nitron and tetraphenylarsonium salts is described together with interesting features of solutions of these compounds. Halogenation of dinitroacetonitrile gave chloro- and bromo-derivatives which have been characterized. The occurrence and isolation of the interestng furoxandinitrile as a product of the nitration of cyanoacetic acid is discussed.

DINITROACETONITRILE was first recognized by Schischkoff[3] in 1861 as the parent acid whose ammonium salt was obtained by reduction of trinitroacetonitrile with hydrogen sulfide. Only a preliminary report was made at that time in which was mentioned the isolation of a crystalline, hydrated dinitroacetonitrile by ether extraction of the acidified ammonium salt. Also mentioned were the identities of potassium and silver salts, obtained by neutralizing solutions of the crystalline hydrate, and the presumed identity of a bromo-derivative obtained by bromination of the silver salt. Reconversion of dinitroacetonitrile into trinitroacetonitrile by nitration was recognized. No other account of further work along these lines has appeared in the literature until this time.

Trinitroacetonitrile has been obtained from the nitration with mixed anhydrous acids of such derivatives of cyanoacetic acid as the acid itself, cyanoacetamide, malononitrile and the nitrosated (oximino) and mono- and dinitro derivatives of each of these (where known). It is presumed that trinitroacetonitrile survives as an end product of rather vigorous nitrating conditions because the three nitro groups effectively drain electrons away from the cyano-group making it resistant toward attack by electrophilic species. The induced positive character of the cyano-group was indicated by its vulnerability toward attack by nucleophilic species including water. Hydrolysis by water during its preparation was minimized by using an oleum containing enough SO_3 to convert all water formed in the reaction to sulfuric acid. Isolation of crystalline trinitroacetonitrile required exposure of personnel to hazards related to its friction and impact sensitivity and its very noxious and toxic vapors. Therefore, a very considerable improvement in the safety aspects and convenience of synthesis of

[1] This research (Parts I to IV) was carried out under Army Ordnance Contract DA-01-021-ORD-5135.
[2] A second method is described in the fourth paper of this series, *Tetrahedron* **17**, 109 (1962).
[3] L. Schischkoff, *Liebigs Ann.* **119**, 250 (1861); *Beil* **2**, 228.

trinitroacetonitrile was realized by carrying out the nitration reaction in the presence of carbon tetrachloride. In CCl_4 solution trinitroacetonitrile could be manipulated safely, assayed and stored or used directly for the preparation of dinitroacetonitrile derivatives.

Cyanoacetic acid was found to be the most satisfactory starting material for the preparation of trinitroacetonitrile. Comparisons of the effect on yield of variations in the ratios of reagents indicated that optimum proportions were very nearly stoichiometric as given by equation (1).

$$NC{-}CH_2{-}COOH + 3HNO_3 + 3SO_3 \xrightarrow{(CCl_4)} (73\text{-}77\%)NCC(NO_2)_3 + CO_2 + 3H_2SO_4 \quad (1)$$

Preparation of dinitroacetonitrile by direct nitration of cyanoacetic acid was investigated by varying the ratio of reagents and reaction conditions. Interpretation of the results of these experiments was predicated upon detection of dinitrocyanomethide ion as the easily purified potassium salt (See Experimental). In no case could this ion be detected by non-reductive neutralization of reaction mixtures. Apparently whatever intermediates intervene in the conversion of cyanoacetic acid to trinitroacetonitrile are transitory in nature and do not accumulate in the reaction mixtures. However, when oximinocyanoacetamide was treated with less than equivalent quantities of nitric acid and the reaction mixture was quenched and neutralized with potassium hydroxide, it was possible to separate and to identify the components as salts of fulminuric acid (nitrocyanoacetamide) and dinitroacetonitrile.

$$NCC(=NOH)CONH_2 + 2HNO_3 \rightarrow [NC{-}CH(NO_2)CONH_2 + NCCH(NO_2)_2] + CO_2 + N_2O + H_2O \quad (2)$$

$$NCC(=NO_2K)CONH_2 + NCC(NO_2)_2K \leftarrow KOH$$

When the mole ratio of nitric acid to cyanoacetic acid was reduced to the vicinity of 2:1 to 1:1 and the amount of sulfuric acid was reduced to catalytic proportions, a new product could be isolated from the reaction mixtures in low yields. This material curiously resembled trinitroacetonitrile closely in appearance, odor and melting point. It was identified as 3,4-dicyanofuroxan[4] by hydrolysis to furoxan-3,4-dicarboxamide.[5] This simple one-step nitration of cyanoacetic acid appears to offer a convenient synthesis of an interesting furoxan derivative which has not been fully investigated.

$$2NCCH_2COOH + 2HNO_2 \xrightarrow[40^\circ]{H_2SO_4} \underset{\text{38\% yield}}{\text{NC{-}C(=N{-}O){-}C(=N{-}O){-}CN}} \quad (3)$$

The reduction of trinitroacetonitrile to dinitroacetonitrile has been effected by numerous reducing agents. Schischkoff used hydrogen sulfide, which was reported to react according to equation (4). Bromide ion was found to function effectively in an acidic ethanol medium. The mechanism and details of this reaction were never fully

$$C(NO_2)_3CN + 4H_2S \rightarrow NH_4^{+\ominus}C(NO_2)_2CN + 4S + 2H_2O \quad (4)$$

elucidated. Neutralization of the entire reaction mixture with various bases gave satisfactory yields of dinitrocyanomethide salts. Contamination by the corresponding

[4] C. Ulpiani, *Gazz. Chim. Ital.* **42**, 1243 (1912); *Chem. Abstr.* **6**, 2235 (1912).
[5] H. Wieland and E. Gmelin, *Liebigs Ann.* **367**, 80 (1909).

trinitromethide salt was minimized if sufficient ethanol and a low enough pH were employed. Sulfur dioxide was found to be serviceable for the replacement of the bulk, but not all of the hydrobromic acid.

For synthetic purposes, sodium dinitrocyanomethide was found to be the most generally useful salt for isolation from the reaction mixture since all other derivatives could be prepared from it. Potassium dinitrocyanomethide was much easier to isolate and to purify due to its sparing solubility in most solvents. (See Table 1.) However,

TABLE 1. SOLUBILITY OF SODIUM AND POTASSIUM DINITROCYANOMETHIDE AT 25°

Solvent	Potassium Dinitrocyanomethide (g/100 g of solution)	Sodium dinitrocyanomethide (g/100 g of solution)
Ethanol	0·09	31·8
Ethyl acetate	0·06	31·5
Acetone	5·97	51·1
Diethyl ether	<0·01	<0·01
Water	4·11	>60

from solutions (usually suspensions) of potassium dinitrocyanomethide attempts to prepare other dinitrocyanomethide salts by metathesis, to isolate dinitroacetonitrile tetrahydrate by acidification with mineral acids or to obtain halodinitrocyanomethyl derivatives were unsuccessful and unreacted potassium salt could be recovered. When reactions were found which did proceed using potassium dinitrocyanomethide, viz., nitration with absolute nitric acid which gave trinitroacetonitrile, dissolution in excess formalin solution which gave some dinitrocyanoethanol[6] and a sulfonic acid ion exchange column[7] which retained all potassium ions and gave an effluate containing dinitroacetonitrile tetrahydrate, it was realized that the unsuccessful reactions failed because of unfavorable equilibrium conditions due to the low solubility of potassium dinitrocyanomethide and the ionic character of the dinitrocyanomethide ion. Other reagents which reacted with potassium dinitrocyanomethide attacked the dinitrocyanomethide ion, as for example, hot aqueous alkali, which gave potassium dinitrothane and alcholic hydrogen chloride which converted it to dinitroacetamide.[8]

The unusual properties of potassium dinitrocyanomethide appear to be derived principally from the equally striking character of the dinitrocyanomethide ion.[9]

[6] Part II: C. O. Parker, W. D. Emmons, A. S. Pagano, H. A. Rolewicz and K. S. McCallum, *Tetrahedron* **17**, 89 (1962).

[7] Rohm & Haas Company Amberlite IR-120.

[8] Part III: C. O. Parker, *Tetrahedron* **17**, 105 (1962).

[9] Nitroform has an acid strength approximating that of phosphoric acid; the yellow color of aqueous-nitroform solutions is readily discharged by addition of mineral acids. It may be presumed that the trinitromethide ion is sterically unable to acquire a planar configuration so that contributions of all possible polar structures to resonance stabilization of the trinitromethide ion are not fully realized. Consequently, only limited resonance energy is lost by the ion in going to covalent trinitromethane.

Sharp contrast is noted with every point of comparison to dinitroacetonitrile. Dinitrocyanomethide salts are very stable thermally compared to trinitromethide salts. No repression of ionization of dinitroacetonitrile solutions by mineral acids could be observed. Covalent dinitroacetonitrile apparently does not exist; instead there was obtained what amounts to a crystalline, solvated dinitrocyanomethide ion, i.e. dinitroacetonitrile tetrahydrate. Finally, solution reactions of dinitrocyanomethide salts gave products derived from all polar structures which might contribute to resonance stabilization of the dinitrocyanomethide ion. (See paper II, this series.) These facts suggest that the best explanation for the distinguishing chemical properties of dinitroacetonitrile may be ascribed to the unique co-planarity and resonance stabilization of the dinitrocyanomethide ion.

Molecular weight and conductivity measurements showed the sodium and potassium salts to be completely ionized in aqueous solution. The equivalent conductances obtained at infinite dilution were 123 ohm^{-1} for the potassium salt, 98 ohm^{-1} for the sodium salt, and 226 ohm^{-1} for the silverpotassium salt. When the equivalent conductances of the cations were subtracted from these values, the conductances at infinite dilution for the dinitroacetonitrile anion in each salt were 49 ohm^{-1}, 48 ohm^{-1}, and 45 ohm^{-1}, respectively. Neither salt could be titrated potentiometrically with perchloric acid in acetic acid solution, which distinguishes them from nitrate salts, for example, and indicates that dinitroacetonitrile is a stronger acid than nitric acid.

TABLE 2. MOLAR EXTINCTION COEFFICIENT $\times 10^{-3}$ [a]

millicrons, mμ	220	232	250	256	288	345	398
Max		7·3		7·0		15·6	
Min	5·4[b]		6·6		1·4		0·5[c]

a Potassium dinitrocyanomethide; all values only approximate, taken from a condensed reproduction.
b Cut-off.
c Tail-off.

The pH of the solution had an inappreciable effect on the dissociation of dinitroacetonitrile, as evidenced by indistinguishable ultraviolet absorption spectra of dinitrocyanomethide salts whether measured in water or in 20 per cent aqueous sulfuric acid solution.

Other dinitrocyanomethide salts which could be prepared by metathesis with aqueous solutions of the sodium salt containing the appropriate cation were: (Melting-decomposition point in parenthesis) Na. anhyd. (226°), K (268°), NH_4 (182°), Ag (196°), nitron (189°) and Ph_4As (177°). From solutions of potassium dinitrocyanomethide containing silver ions a silver–potassium double salt crystallized upon cooling, m.p. 224°. The 1:1 mole ratio of silver to potassium in the salt which crystallized was unaffected by the solvent. Halide ions precipitated the silver.

Dinitroacetonitrile itself was never isolated in pure, anhydrous condition. However, hydrated dinitroacetonitrile fortuitously showed appreciable solubility in ethyl ether and from ether solutions colorless crystalline products could be isolated. The melting point of this material varied from 37–40° depending upon the preparation; it was insoluble in non-polar solvents and gave neutral equivalents, elementary analyses, and water determinations (Karl Fischer) which were in agreement with several dinitroacetonitrile hydrates. The amount of water present varied somewhat, but each preparation gave good analytical data, water analysis, and neutral equivalent for a particular hydrate. All samples contained three to four moles of water per mole of dinitroacetonitrile. Attempts to remove the water gave crude products having neutral equivalents ranging down to 144 (pure dinitroacetonitrile, 131). Distillation of dinitroacetonitrile hydrate, under reduced pressure produced in part, decomposition to nitric acid. The crystalline tetrahydrate was quite stable when kept cold, and no loss of water took place after five days evacuation over phosphorous pentoxide at 0°. On the other hand, samples stored at room temperature at atmospheric pressure softened and discolored within two days. Sodium dinitrocyanomethid itself formed a

stable monohydrate (m.p. 214–216°) on exposure to normal laboratory atmosphere (50 per cent relative humidity). Although anhydrous dinitroacetonitrile could not be islolated as such, essentially anhydrous solutions of dinitroacetonitrile in various solvents were prepared by neutralizing suspensions of anhydrous sodium salt with an equi-molar quantity of sulfuric acid. Such solutions were stable enough for immediate synthetic use. All of the aforementioned properties of dinitroacetonitrile, its existence as a crystalline hydrate and its instability when the water of hydration was removed, its apparent complete dissociation in strong mineral acid solution, strengthen the impression that dinitroacetonitrile would best be represented as hydronium dinitrocyanomethide.

VOL. 17 1962

TABLE 3. MOLECULAR WEIGHTS OF SODIUM AND POTASSIUM DINITROCYANOMETHIDE

Salt	$NaC(NO_2)_2CN$	$KC(NO_2)_2CN$
Theor. mol. wt. (2 ions per mole)	76·5	84·5
Cryoscopic in water	75·5	83·9
Ebullioscopic in water	75·3	88·9
Ebullioscopic in acetone	104·0	116·1
Fraction dissociated in acetone	0·74	0·73

The only covalent derivatives of dinitroacetonitrile to be considered in this paper are the nitro- and halogen-derivatives; others are described in the succeeding papers. Trinitroacetonitrile as mentioned above, could be obtained rather easily by nitration of dinitroacetonitrile or its salts. A sort of autonitration or disproportionation reaction was observed to take place when dinitroacetonitrile tetrahydrate was suspended in excess cold, concentrated sulfuric acid and cold, fuming sulfruic acid was added: trinitroacetonitrile slowly sublimed away from the liquid phase and condensed on the vessel walls. Nucleophilic attack on trinitroacetonitrile has been observed to take place in two ways: hydroxide ion, which requires a very high oxidation potential, appears to attack the cyano-group and give trinitromethide salts and cyanate ion in good yield, depending on the conditions. More easily oxidized agents (or media) may be presumed to undergo a one-electron transfer to give the very stable dinitrocyanomethide ion.

The halogen derivatives, chloro- and bromo dinitroacetonitrile, were prepared readily by halogenation of solutions of sodium dinitrocyanomethide. A superior method of preparation of chlorodinitroacetonitrile was found to consist in oxidation of solutions of sodium dinitrocyanomethide in hydrochloric acid with hydrogen peroxide, thereby avoiding contamination of the chloroderivative with much excess free chlorine. Application of this method to the preparation of the bromo-derivative was never attempted. Investigation of the chemistry of these compounds was very limited. Attempts to bring about addition of bromodinitroacetonitrile to ethylene and to cyclohexene failed to yield dinitrocyanomethyl adducts.

EXPERIMENTAL

Trinitroacetonitrile[10]

Cyanoacetic acid, 340 g (4 moles), was suspended in 1000 ml of carbon tetrachloride in a 12 l., three-necked, round-bottom flask equipped with a thermocouple, a mechanical stirrer, a 1 l. funnel and a Dry Ice cooled condenser. The latter two items were attached to the flask by means of a 'Y' tube and each was protected from atmospheric moisture by means of a calcium chloride drying tube. The contents of the flask were cooled to 0°C, and 630 ml (13·5 moles) of white fuming nitric acid, d. 1·49–1·50, was introduced rapidly by means of the addition funnel. Seven hundred and fifty milliliters of 27% fuming sulfuric acid (16 moles) were poured into the addition funnel and then with a Dry Ice–isopropanol bath strategically placed beneath the flask, the entire quantity of acid was added by remote control as rapidly as it would flow from the funnel (usually about 5–6 min) while the temperature of the reaction mixture was maintained below 10°. The temperature of the reaction mixture was allowed to rise to 25° and was kept at this level for 80 min. It was then allowed to rise to 30° where it remained for about ½ hr by spontaneous, but slow, evolution of heat. The mixture was then cooled to about 10° and poured into a 3 l. separatory funnel. The lower, mixed acid layer was separated from the carbon tetrachloride layer and extracted with a 300 ml portion of carbon tetrachloride. The carbon tetrachloride solutions were combined and shaken with two 250 ml portions of ice cold 70% sulfuric acid. On separation from the last of these acid solutions, a colourless to light yellow carbon tetrachloride solution of trinitroacetonitrile (73–77% yield) was obtained. When the solution was to be stored for an extended period of time, about 25 g of anhydrous magnesium sulfate was added to the solution to insure desiccation.

TABLE 4. TIME REQUIRED FOR HYDROLYSIS OF TRINITROACETONITRILE

	Concentration of trinitroacetonitrile (g/100 ml.) determined after		
Sample No.	¼ hr	½ hr	1 hr
1	25·5	25·7	25·5
2		25·7	25·5

TABLE 5. GRAMS TRINITROACETONITRILE FOUND PER 100 ml OF SOLUTION

Sample no.	Gravimetric method	Ultraviolet method	Infrared method
1	23·14	23·0	23·3
2	30·22	30·1	30·8
3	32·88	32·6	33·3
4	24·97	24·3*	25·3
5	26·08	25·9	26·6
6	23·84	23·6	23·6

* This figure is the average of four measurements; all others are the average of two measurements.

Analysis of Trinitroacetonitrile

The best results were obtained when trinitroacetonitrile in carbon tetrachloride solution was hydrolyzed by stirring with excess aqueous alkali for approximately 15 min (Table 4). The trinitromethide

[10] *Warning*

All manipulations of trinitroacetonitrile, trinitromethyl and dinitrocyanomethyl derivatives were performed either remotely (quantities greater than 25 g) or from behind the protection of safety shields tested for resistance to detonation of 25 g charges of explosive at distances of not less than eight inches. The same precautions were observed with storage of samples. All melting point baths were enclosed in Plexiglas cabinets, since rupture of a melting point apparatus occurred more than once. All personnel were required to wear safety glasses with side guards upon entering the laboratory area.

salt was then determined either gravimetrically with tetraphenylarsonium chloride or by measuring the optical absorption of an appropriate dilution at 350 mμ.

An alternative, very rapid method was based on measuring the optical absorption of the nitrile band at 2250 cm^{-1}. This method allowed direct use of the carbon tetrachloride solution or a singly diluted solution. Table 5 shows the agreement obtained with these three methods.

The gravimetric procedure was believed to be the most precise because the per cent error involved in weighing is very much less than that involved in the spectrophotometric methods. The infrared method was certainly the fastest and probably the least sensitive to contaminants.

As regards the determination of trinitromethide ion using tetraphenylarsonium chloride, the effect of varying the volume of solution from which the tetraphenylarsonium trinitromethide is precipitated was studied. Changes of volume between 20 ml and 155 ml were without significant effect on the results.

VOL. 17 1962

The precision of the gravimetric procedure was tested by analysis of ten aliquots from a single nitroform solution. Results ranged from 97·64% to 100·82%, average 98·45%, standard deviation 1·05% based on the weighed nitroform. Since this work was done during the familiarization period, it is expected that the method is capable of more precise results.

The precision of the ultraviolet absorption method could probably be improved by a differential measurement using a standard solution for the initial instrument setting. Potassium trinitromethide was first tried as a standard solution. Solutions of the order of 10^{-3} molar were found to be stable for two weeks; stronger solutions were quite unstable. Solid ammonium trinitromethide and aqueous 0·1 and 0·01 M solutions of ammonium trinitromethide were stable for at least three weeks within the limits of detection by ultraviolet absorption.

Sodium Dinitrocyanomethide

To a mechanically stirred solution of 600 ml of 48% hydrobromic acid in 1700 ml of ethanol contained in a three-necked, 12 l. flask was added a solution of trinitroacetonitrile (the total product of a 4 mole run) in approximately 1600 ml of carbon tetrachloride. The temperature of the reaction mixture slowly increased to about 50–55°, and remained there for approximately 1 hr. During this time the solution became red, then brown, and finally black; brown fumes resembling bromine were quite evident. It has also been observed that ethyl nitrite is one of the major by-products of this reaction, and therefore adequate ventilation must be provided in the vicinity of the reaction vessel. When the evolution of heat ceased, the solution was cooled to 0–5° and was neutralized with sufficient 3 N methanolic sodium hydroxide to raise the pH value to 8. Addition of base caused the solution gradually to become red, orange, and finally at the desired pH value, a very light yellow. A small quantity of precipitated sodium bromide usually made its appearance during the neutralization step. The solvent was then distilled from the reaction mixture at reduced pressure and the dry residue was extracted with two 500 ml portions of ethyl acetate. The ethyl acetate solution of sodium dinitrocyanomethide was treated with decolorizing charcoal and the salt was precipitated by addition of 2 l. of ether. The sodium dinitrocyanomethide, 360–400 g (59–65%), was separated by filtration and dried in a vacuum oven at 70–80° for 4 hr. Its melting point (decomposition) was 224–226°.

(Found: Na, 13·96. Calc. for $NaC(NO_2)_2CN$. H_2O, m.p. 214–216°, recrystallized from ethyl acetate benzene solution; Na, 13·45.)

(Found: Na, 15·36. Calc. for $NaC(NO_2)_2CN$. Na, 15·03.)

Potassium Dinitrocyanomethide

The preparation of potassium dinitrocyanomethide was identical with that of the sodium salt with the exception that methanolic potassium hydroxide was substituted for sodium hydroxide. The work-up of the salt was considerably simplified by the fact that potassium dinitrocyanomethide was insoluble in the solvent system in which it was formed. Potassium dinitrocyanomethide and potassium bromide, which was equally insoluble, were isolated on a filter.[11] The mixture of salts (800–900 g) was dried for 6 hr at 70–80° in a vacuum oven and then transferred to a 1500 ml. Soxhlet extractor and extracted with 2 l. of acetone over a 12 hr period.

Most of the potassium dinitrocyanomethide, which is only moderately soluble in acetone, was

[11] This salt mixture could be triturated with cold water, refiltered, washed with cold water and the filter cake recrystallized from water without losing prohibitive quantities of the potassium dinitrocyanomethide originally present.

filtered from the acetone in the distillation flask at this time. The balance was precipitated by the addition of about 1 l. of ether to the acetone solution which had been previously concentrated to one-fourth of its original volume. By this procedure there was obtained 455–500 g (67–75%) of potassium salt which melted with decomposition at 262–264°.

Crude salt recrystallized from water exhibited a yellow color. It could be suspended in 85% phosphoric acid and stirred overnight, filtered, washed with ethanol and recovered in pure, white condition. The same treatment using concentrated hydrochloric acid or recrystallization from 20% aqueous sulfuric acid also helped remove yellow coloration.

(Found: K, 22·99. Calc. for $C_4O_4N_3K$: K, 23·12.)

Silver-Potassium Dinitrocyanomethide Double Salt

Potassium dinitrocyanomethide was dissolved in an aqueous solution containing a two-fold excess of silver nitrate. The product which crystallized on cooling the solution was recrystallized from fresh aqueous silver nitrate solution and then twice from distilled water, m.p. 224°. When this product was dissolved in acetone and precipitated by the addition of ether, the silver content was unchanged.

(Found, Ag, 26·48. Calc. for $C_4O_4N_4AgK$: Ag, 26·51.)

Dinitroacetonitrile Polyhydrate

Thirty-two and four-tenths grams of sodium dinitrocyanomethide (0·211 mole) was dissolved in 17·5 ml of water, and the water layer was covered with 60–70 ml of ether. The mixture was stirred in a cooling bath and 20·7 g (0·21 mole) of concentrated sulfuric acid was added dropwise. There was no resulting aqueous layer, and the ether was decanted from the moist salt. Extraction with ether was continued in portions until the extracts became colourless. The ether extracts were dried overnight with anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residual crystalline solid was washed onto a filter with methylene chloride. After evacuation in a desiccator there was obtained 25·3 g of white crystals m.p. 37–40·5°. The water content of this material was determined by Karl Fisher titration.

(Found: Neut. equiv., 186·7; H_2O, 31·0. Calc. for $C_2HN_3O_4$, 3·25H_2O: Neut. equiv., 188·5; H_2O, 31·1.)

When a similarly prepared product was transferred from the filter directly to a flask and was sublimed at 20°/1·0 mm, a white crystalline product was obtained in an ice-cooled receiver. This sublimate had the composition of a tetrahydrate, m.p. 37–40°.

(Found: C, 12·42; H, 4·26; N, 19·89; neut. equiv., 202·0. Calc. for $C_2HN_3O_4$, 4 H_2O: C, 11·82; H, 4·43; N, 20·69; neut. equiv., 203·1.)

Continued distillation of the residue (treated with 1% diphenylamine) gave a liquid fraction. This was redistilled twice and was finally found to be mostly nitric acid, as indicated by the melting point of its nitron derivative (m.p. 263°).

All preparations of the initial crystalline product, whether the mineral acid employed was sulfuric, hydrochloric, or phosphoric acid, yielded nitron derivatives which, after recrystallization from ethanol, melted at 189–190°, and gave no depression in melting point when mixed with a derivative prepared directly from samples of crystalline hydrate which had liquefied after evacuation overnight in the presence of concentrated sulfuric acid. Distillation of this liquefied material, however, produced decomposition even at low temperatures.

Silver Dinitrocyanomethide

A solution of 116·2 g (15% molar excess) of silver nitrate in 40 ml of water was added to a solution of 70·5 g (0·46 mole) of sodium dinitrocyanomethide in 80 ml of water at 40°. The suspension of silver salt was cooled, filtered and washed with cold ethanol. The product was recrystallized from 300 ml of water heated to 90° and filtered while hot, giving 67·4 g (61·5% yield) of silver dinitrocyanomethide. The salt exploded at 196° in a capillary melting point tube and shattered the apparatus. It is soluble in acetonitrile, water and acetone and insoluble in alcohols.

(Found: Ag, 44·92. Calc. for $C_2O_4N_2Ag$: Ag, 45·33.)

Bromodinitroacetonitrile

Sodium dinitrocyanomethide (9·0 g, 0·059 mole) was dissolved in a mixture of 9 ml of water and 13 ml of methylene chloride. Calcium carbonate (5 g) was suspended in the mixture, which was

stirred vigorously at 0–5°. Bromine (3 ml, 0·059 mole) was added to the mixture dropwise. The organic layer was separated and dried with magnesium sulfate. After removal of drying agent and solvent, the residue was distilled and two fractions were collected: (1) 1·6 g, 40°/5–10 mm, n^{23} 1·4832; (2) 2·7 g (22%), 35–36°/4 mm, n_D^{23} 1·4860. Fraction (2) was titrated iodimetrically and found to contain 96% bromodinitroacetonitrile (positive bromine). The infrared spectrum of this material contained nitrile and dinitrocyanomethyl absorption bands at 2240 cm^{-1} and 1608^{-1}, respectively.

Chlorodinitroacetonitrile

Thirty-three grams (0·19 mole) of sodium dinitrocyanomethide monohydrate was added in one portion to a stirred mixture of 70 ml of concentrated hydrochloric acid and 70 ml of 30% hydrogen peroxide at 30°. The reaction temperature was maintained at 33–35° for 2 hr by the intermittent application of an ice bath. During this interval, a colorless oil separated from the solution. The mixture was cooled to about 5° and the two layers separated. The product was washed once with a 15 ml portion of water and was dried over calcium chloride to yield 30·8 g of chlorodinitroacetonitrile. The product rapidly became yellow on standing at room temperature. Distillation of the crude product (b.p. 38°/14 mm) yielded 29·0 g (91%) of chlorodinitroacetonitrile, n_D^{20} 1·4509.

3,4-Dicyanofuroxan

Seventeen grams (0·2 mole) of cyanoacetic acid was dissolved in 50 ml of trifluoroacetic acid magnetically stirred in a 250 ml three-necked flask equipped with a thermometer, drying tube-closed water condenser and a stoppered, pressure-equalized 25 ml dropping funnel. Fifteen and eight-tenths grams (0·25 mole) of anhydrous nitric acid was placed in the dropping funnel. The reaction mixture was warmed to 40° and slow dropwise addition of the nitric acid was begun. After 1 ml had been added, 0·5 ml of 30% fuming sulfuric acid was added from a pipette through the condenser. About 2 hr elapsed during the addition of nitric acid, during which time the reaction temperature was held at 40° ± 5°. Soon after the acid was all added the solution was cooled and poured with stirring over 200 g of ice and water. The quenched mixture was extracted with two 20 ml portions of methylene chloride. The combined extracts were washed with cold water until neutral and dried with sodium sulfate. Solvent was evaporated and the residue (which is rather volatile) was triturated with carbon tetrachloride, causing it to crystallize. The white crystals were filtered, washed with cold carbon tetrachloride and recrystallized from just enough carbon tetrachloride to give a solution at 40°. Cooling this solution gave 5·2 g (38% yield) of crisp, white product, m.p. 42°. The product sublimed rapidly onto a Dry Ice cooled cold finger when heated to 35°/0·1 mm. Its infrared spectrum contained clean, sharp bands at the following frequencies, all of which, except the cyano-(2227 cm^{-1}) correspond to characteristic vibrations of the furoxan ring recognized by Boyer *et al.*[12] 2227, 1637, 1460, 1305, 1104, 1045, 844, 745, 688 cm^{-1}, (capillary melt spectrum). Elementary analysis of this material ($C_4O_4N_4$) gave consistently low values for nitrogen which made the analysis valueless.

Furoxan-3,4-Dicarboxamide

Four-tenths grams of sublimed dicyanofuroxan was dissolved in 5 ml of concentrated sulfuric acid at room temperature and the solution was left idle overnight. The colourless solution was poured onto 25 g of crushed ice causing precipitation of white solid material. The product was collected on a filter, washed with ice-water until the washes were neutral and recrystallized from hot water, m.p. 233°.[13]

[12] N. E. Boyer, G. M. Czerniak, H. S. Gutowsky and H. R. Snyder, *J. Amer. Chem. Soc.* 77, 4238 (1955).
[13] H. R. Snyder and N. E. Boyer, *J. Amer. Chem. Soc.* 77, 4233 (1955), report m.p. 232°.

Tetrahedron, 1962, Vol. 17, pp. 89 to 104. Pergamon Press, Ltd. Printed in Northern Ireland

VOL. 17 1962

CHEMISTRY OF DINITROACETONITRILE—II

DERIVATIVES OF DINITROACETONITRILE FROM MICHAEL, MANNICH AND ALKYLATION REACTIONS. 2,2-DINITRO-2-CYANOETHANOL AND ITS DERIVATIVES

CHARLES O. PARKER, WILLIAM D. EMMONS, ANGELO S. PAGANO, HENRY A. ROLEWICZ and KEITH S. MCCALLUM
Rohm & Haas Co., Redstone Arsenal Research Division
Huntsville, Alabama

(*Received* 23 *March* 1961)

Abstract—Addition of dinitroacetonitrile to carbonyl conjugated unsaturated systems was a generally successful reaction for the preparation of Michael adducts. The expected products were obtained with methyl acrylate, acrylamide, acrolein, butenone, methylene-bis-acrylamide, and N,N′,N″-triacrylylperhydro-s-triazine. Acrylic acid gave three products: the normal adduct, the corresponding carbamyl derivative and its cyclic imide.

Dinitrocyanoethanol was easily prepared by reaction of dinitroacetonitrile with formaldehyde and the acetate, trifluoroacetate, acrylate and methacrylate esters of this alcohol were characterized. Esterification with 3,5-dinitrobenzoylchloride, fumaryl chloride and succinyl chloride gave liquid esters which could not be purified.

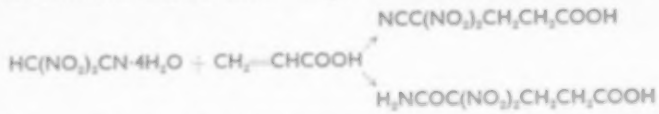
N-(2,2-Dinitro-2-cyanoethyl)amides could be prepared in relatively general fashion as the products of reaction of dinitroacetonitrile with N-methylolamides. The corresponding acetyl, benzoyl, acrylyl, methacrylyl and bis-urea derivatives are described. These compounds were sensitive toward hydrolysis.

Alkylation of dinitroacetonitrile and its salts to give identifiable products was not generally successful. As special cases the C-allyl, O-methyl, C-t-butyl and N-t-butyl derivatives could be prepared and were characterized.

DERIVATIVES of dinitroacetonitrile in which the dinitrocyanomethyl group was covalently linked via a carbon–carbon bond were found to be obtained from three different types of reaction. Of these, addition of dinitroacetonitrile tetrahydrate to carbonyl-conjugated double-bond systems was the most generally successful product producing type of reaction studied. The resulting Michael adducts were obtained in good yields, were relatively easily purified and were no more susceptible toward hydrolysis and adventitious decomposition of the dinitrocyanomethyl group than were the carbon-substituted alkyl derivatives. The presence of β-carbonyl groups complicated the infrared spectra of these molecules and also their behavior in alkaline decomposition reactions but on both counts these complications were less troublesome than those encountered in dealing with other types of derivatives. The Michael adducts prepared have been listed in Table 1 together with data pertinent to the reactions and products.

A curious feature of dinitroacetonitrile chemistry which was encountered was the variety of products obtained from the Michael addition reaction of dinitroacetonitrile with acrylic acid. These were identified as the expected normal adduct, 4,4-dinitro-4-cyanobutyric acid, which was a minor rather than a principal product and 4,4-dinitro-4-carbamylbutyric acid, which was the principal product of the reaction in aqueous

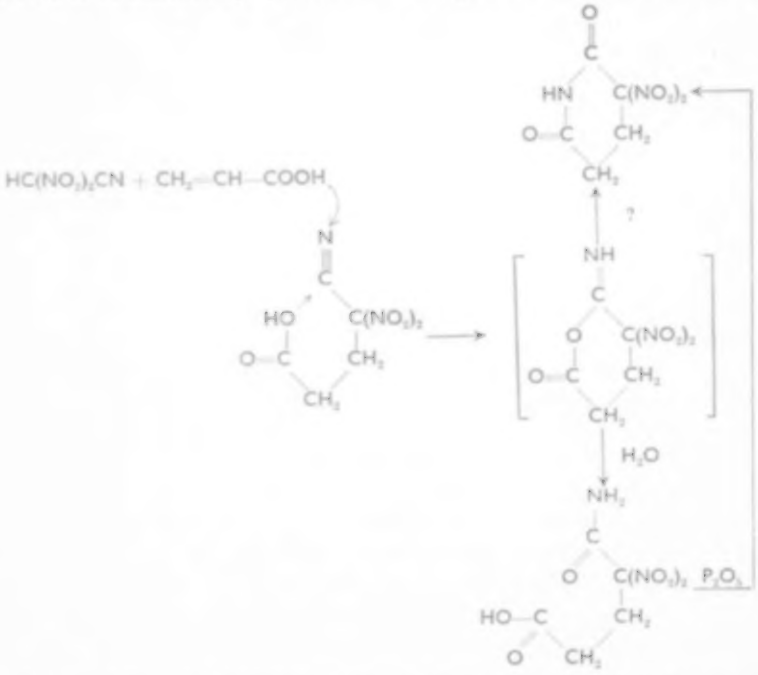
media and even when the addition was performed in t-butyl alcohol solution.[1] For-



mation of the carbamyl adduct cannot be attributed to secondary hydrolysis of the normal adduct through the agency of the water present in dinitroacetonitrile tetrahydrate because Michael addends other than acrylic acid showed no sort of corresponding behavior (see Table 1).

When acrylic acid was treated with anhydrous dinitroacetonitrile in ethyl acetate solution a product was obtained which was isomeric with the normal adduct and which was designated as α,α-dinitroglutarimide on the basis of its infrared absorption characteristics, elementary analysis and alternative preparation by treatment of the above carbamyl derivative with P_2O_5.

This diversity of related products obtained from the acrylic acid-dinitroacetonitrile reaction may be accounted for most readily by postulating cyclization of the normal adduct (4,4-dinitro-4-cyanobutyric acid) resulting from intramolecular nucleophilic attack of the carboxyl group on the electron deficient cyano-group, i.e. the site which was observed to be attacked by hydroxide ion in degradation experiments (see below):

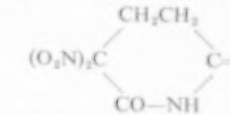
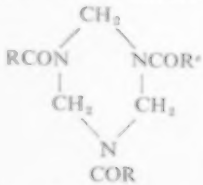
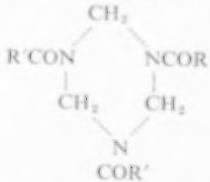


The relationship between the postulated cyclic intermediate (bracketed structure) and the α,α-dinitroglutarimide structure remains unresolved. If it were not for the experimental observations that, firstly, the carbamyl-adduct was obtained copiously through the evident agency of relatively little water in the reaction mixture, and

[1] Use of t-butyl alcohol avoided esterification of the carboxyl group.

VOL. 17 1962

TABLE 1. MICHAEL REACTIONS OF DINITROACETONITRILE

Michael addend	Dinitroacetonitrile	Solvent	Reaction		Product	m.p. b.p.	Product % yield
			hr.	temp.			
CH_2=CHCOOMe	tetrahydrate	methanol	5	60°	$(O_2N)_2C(CN)CH_2CH_2COOMe$	78–80°/0·12–0·15 mm	21
CH_2=$CHCONH_2$	anhydrous[a]	ether	24	36°	$(O_2N)_2C(CN)CH_2CH_2CONH_2$	62–63°	29
CH_2=CHCOOH	tetrahydrate	water	15	35°	$(O_2N)_2C(CN)CH_2CH_2COOH$	73–74°	13
			16	25°	$(O_2N)_2C(CONH_2)CH_2CH_2COOH$	115–117°	60
CH_2=CHCOOH	tetrahydrate	t-butanol	14	40°	$(O_2N)_2C(CONH_2)CH_2CH_2COOH$	111–113°[b]	69
CH_2=CHCOOH	anhydrous[a]	ethyl acetate	12	40°		146–148°	34
CH_2=CHCHO	tetrahydrate	water	40	25°	$(O_2N)_2C(CN)CH_2CH_2CH(OCH_3)_2$[c]	80–81°/0·4 mm	57[d]
$(CH_2$=$CHCONH)_2CH_2$	tetrahydrate	water	7	55°	$[(O_2N)_2C(CN)CH_2CH_2CONH]_2CH_2$	133–134°	51
	tetrahydrate	methanol	15	40°		140–141°	26
CH_2=$CHCOCH_3$	tetrahydrate	water	120	25°	$(NO_2)_2C(CN)CH_2CH_2COCH_3$	75/0·2 mm[e]	68

[a] Prepared *in situ* by neutralizing the sodium salt with sulfuric acid.
[b] No depression in mixed melting point with product of m.p. 115–117°.
[c] After subsequent reaction of crude product with methyl orthoformate.
[d] Yield of crude acetal.
[e] R = (CH_2=CH_2—).
[f] R′ = [$(O_2N)_2C(CN)CH_2CH_2$—].
[g] In falling film still.

secondly, that the product designated as α,α-dinitroglutarimide was relatively unaffected by water (see Experimental) it would be tempting to conclude that the dehydro-product actually possessed the imino-anhydride structure. A more sophisticated structure elucidation was not feasible at the time this work was in progress.

The Michael adduct obtained from methyl acrylate could be hydrolyzed quantitatively to succinic acid.

$$(NO_2)_2C(CN)CH_2CH_2COOCH_3 \xrightarrow[H_2O]{HCl} HOOCCH_2CH_2COOH$$

Although attempts to prepare a Michael adduct of dinitroacetonitrile with acrylonitrile were unsuccessful, this product was obtained by dehydration of 4,4-dinitro-4-cyanobutyramide in 30% yield.

$$(NO_2)_2C(CN)CH_2CH_2CONH_2 \xrightarrow{P_2O_5} (NO_2)_2C(CN)CH_2CH_2CN$$

Reaction of dinitroacetonitrile with formaldehyde yielded 2,2-dinitro-2-cyanoethanol, a genuine carbon-alkylation product. This derivative was easily prepared but less easily purified since it tended to retain excess formaldehyde and to undergo retrogression.

$$HC(NO_2)_2CN + CH_2O \rightleftharpoons (NO_2)_2C(CN)CH_2OH$$

A number of esters of dinitrocyanoethanol were prepared. These included the trifluoroacetate, acetate, acrylate, and methacrylate. The acetate and methacrylate were obtained by reaction of the alcohol with the appropriate acid in the presence of trifluoroacetic anhydride as the condensing agent.

$$CH_2{=}C(CH_3)CO_2H + HOCH_2C(NO_2)_2CN \rightarrow CH_2{=}C(CH_3)CO_2CH_2C(NO_2)_2CN$$

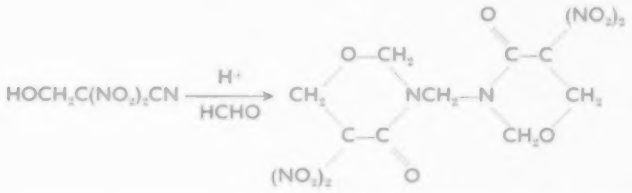
All of the esters of dinitrocyanoethanol were noticeably fragile toward moisture catalyzed decomposition. Bulk polymerization of the methacrylate with azo-bis-isobutyronitrile as the catalyst gave a hard but somewhat discolored polymer. An attempt to prepare the methacrylate by azeotropic distillation of water from a mixture of 2,2-dinitro-2-cyanoethanol and anhydrous methacrylic acid in benzene gave a quantitative yield of water but a polymerized product. The mixed anhydride technique was also used to obtain 2,2-dinitro-2-cyanoethyl acrylate, but even careful fractionation failed to separate completely the acrylate from the trifluoroacetate formed in the esterification reaction. However, a pure sample of the acrylate was obtained in 49 per cent yield by esterification of 2,2-dinitro-2-cyanoethanol with acrylyl chloride in the presence of aluminum chloride; this procedure proved to be the more satisfactory one for the methacrylate. Bulk polymerization of both monomers with azo-bis-isobutyronitrile gave a gummy mass.

Esterification of 2,2-dinitro-2-cyanoethanol with fumaryl chloride, succinyl chloride and 3,3-dinitrobenzoyl chloride gave in each case a liquid product which on the basis of infrared examination appeared to be the desired ester. However, these liquids

could not be crystallized even at Dry Ice temperatures and all decomposed on attempted distillation.

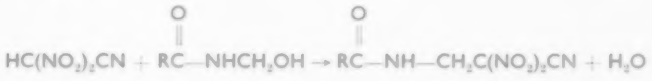
Nitration of 2,2-dinitro-2-cyanoethanol with a mixture of concentrated nitric and sulfuric acids gave a 67 per cent yield of a liquid which on the basis of its infrared spectrum appeared to be largely the desired nitrate ester. It was possible to distill this product and a fraction boiling at 46–55°/1 mm showed the expected nitrate absorption band at 1678 cm^{-1} and the dinitrocyanomethyl band at 1600 cm^{-1}. The nitrogen value obtained on elemental analysis was low, however, indicating the material was impure. The product appeared to be quite unstable since a sample became acidic fairly rapidly on standing. For this reason work with this compound was abandoned.

When an attempt was made to hydrolyze the nitrile group in 2,2-dinitro-2-cyanoethanol with concentrated sulfuric acid a product was isolated in fair yield which was believed to be a cyclic methylene-bis-amide. It was established that this product was formed by a reaction with the excess formaldehyde dissolved in the dinitrocyanoethanol, and the same product was obtained in much better yield when additional formaldehyde was used.



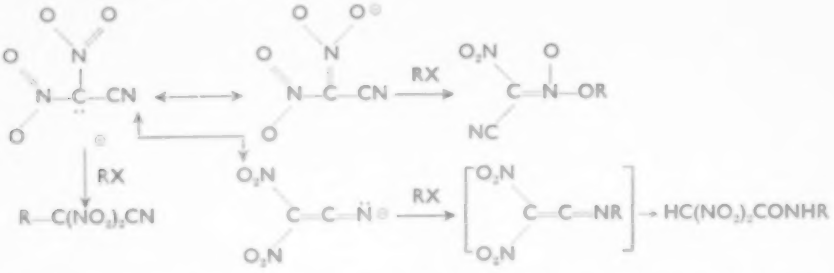
The analysis, infrared spectrum, and solubility properties of this product were in agreement with the proposed structure.

Several attempts were made to prepare Mannich-type derivatives through reaction of dinitrocyanoethanol with amides and ammonium salts. In several instances unelucidated interaction took place, but no dinitrocyanomethyl-derivatives could be prepared in this way. Under rather limited environmental conditions N-(2,2-dinitro-2-cyanoethyl) amides could be prepared through the reaction of dinitroacetonitrile with N-methylolamides.



In most cases successful isolation of product seemed to depend upon choice of a relatively non-polar solvent medium, such as ethyl acetate, the presence of a drying agent to remove water formed in the reaction and judicious separation of excess reactants. Dinitrocyanoethylamides showed a much greater proclivity toward solvolysis than esters of dinitrocyanoethanol. In the presence of strong base however, a competitive type of direct attack on undissociated dinitrocyanoethylamide was observable. Thus when dinitrocyanoethylacetamide was dissolved in cold aqueous ethanol and was titrated immediately, neutral equivalent values as low as 137 were obtained. If complete preliminary hydrolysis were insured by warming the solution on the steam bath or allowing it to stand overnight before titration, values in good agreement with the theoretical neutral equivalent (202) were obtained.

Reactions of the dinitrocyanomethide ion with organic halides gave products which represented covalent bond formation derived from all three possible contributing structures of the ion:



Of the organic halides which were investigated only methyl, allyl and t-butyl halides gave rise to stable, isolable products. Of these only allyl and t-butyl produced carbon-alkylated products. Since the same products which were isolated from alkylation of silver dinitrocyanomethide with t-butyl halide were also formed in reactions of t-butyl alcohol with dinitroacetonitrile tetrahydrate, it seems evident that these reactions were functions of the t-butyl carbonium ion. The structure of the products, then, reflected indiscriminate attack of the t-butyl carbonium ion on at least two of the three contributing structures of which the dinitrocyanomethide ion consists. A third, unidentified product was formed in these reactions which may or may not have been derived from an intermediate t-butyl nitronate. Fortunately the mixture of carbon and nitrogen t-butyl alkylated products was easily separated by making use of the difference in their chemical properties. The carbon alkylated product, 2,2-dinitro-3,3-dimethylbutyronitrile, was most easily soluble in non-polar solvents and unaffected by mild exposure to aqueous acids and bases. The nitrogen alkylated product emerged from reaction mixtures as N-t-butyl-α-α-dinitroacetamide, easily soluble in dilute aqueous alkali and insoluble enough in water to be precipitated by acidification.

Methyl iodide reacted with silver dinitrocyanomethide in most solvent systems. The best yields of stable, isolable product were obtained from heterogeneous mixtures containing silver salt suspended in excess methyl iodide. Identification of this product as the oxygen alkylated derivative was finally made on the basis of its ultraviolet absorption spectrum, which showed a strong maximum near 300 mμ, and from study of its hydrolysis products from acidic and basic solutions. The nitronate structure gave absorption bands in the 6 μ region of its infrared spectrum which could be ambiguously interpreted. However, the above-mentioned bona fide carbon alkylated derivatives were sharply distinguished by the absence of long wave length ultraviolet absorption. The nitronate structure was further corroborated by solvolytic fragmentation into dinitrocyanomethide ions and formaldehyde.

It was observed quite early in the work with organic derivatives of dinitroacetonitrile that most of these compounds had reproducible neutral equivalents and could be titrated with base. Generally two equivalents of base were consumed per mole of dinitrocyanomethyl groups and in most cases the titration could be carried out with sodium hydroxide to a phenolphthalein end point (Table 2).

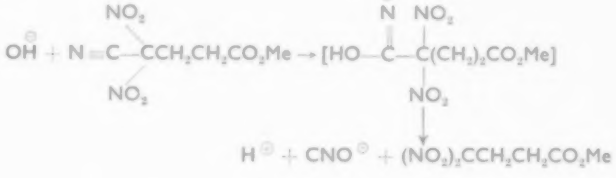
The behavior of methyl 4,4-dinitro-4-cyanobutyrate with base was studied in some detail. The ester reacted rapidly with methanolic potassium hydroxide, potassium

cyanide, or sodium methoxide to give in each case quantitative yields of a yellow solid which was recrystallizable from hot methanol. This material proved to be the potassium salt of methyl 4,4-dinitrobutyrate. Repeated recrystallization of the salt resulted in an analytically pure sample which was converted to the distillable dinitro compound,

TABLE 2. NEUTRAL EQUIVALENTS OF DINITROCYANOMETHYL DERIVATIVES

Compound	MW	Neut. equiv.	Equivalents used per mole
$NCC(NO_2)_2(CH_2)_2COOH$	203	68·6	3
$NCC(NO_2)_2(CH_2)_2COOCH_3$	217	105·8	2
$NCC(NO_2)_2(CH_2)_2CONH_2$	202	105·0	2
$NCC(NO_2)_2CH_2OC(=O)C(CH_3)=CH_2$	229	113·5	2

methyl 4,4-dinitrobutyrate. This material was characterized by reaction with methyl acrylate to give dimethyl 4,4-dinitropimelate, m.p. 46°. The inorganic residue from the alkaline degradation was examined and found to contain mostly potassium cyanate. Thus the overall reaction appears to involve nucleophilic attack on the nitrile group.



EXPERIMENTAL

Alkylation Products of Dinitroacetonitrile 4,4-*Dinitro*-4-*Cyanobutene*-1

To a solution of 28·7 g (0·12 mole) of silver dinitrocyanomethide in 300 ml of acetonitrile was added 18·0 g (0·148 mole) of allyl bromide. After heating at 40–45° for 3 hr, 9·2 g of silver bromide was isolated. An additional 2 g of allyl bromide was added to the reaction mixture and after heating for 4 hr at 40–60° another 7·6 g of silver bromide was obtained. Five grams of allyl bromide was added, and the solution was allowed to stand for two days. Altogether 21·1 g (94%) of silver bromide was collected. Most of the solvent was removed under reduced pressure. The residue was dissolved in ether, washed with water, with 5% sodium bicarbonate solution, with water again, and was then dried with anhydrous magnesium sulfate. After removal of solvent there remained 10·4 g of residue. This was flash distilled from a bath at 85–90° at 0·5–1·5 mm to yield 7·1 g (35%) of crude 2,2-dinitro-4-pentenenitrile, n_D^{20} 1·4558. This material was fractionally distilled through a Holtzman Column. A 3·5 g portion which distilled at 38–40°/0·4 mm was analyzed and its infrared spectrum measured, n_D^{20} 1·4552.

(Found: C, 34·63; H, 2·67; N, 23·77. Calc. for $C_5H_5O_4N_3$: C, 35·08; H, 2·92; N, 24·56.)

"*Methyl Dinitroacetonitrile*," *Dinitroacetonitrile*-O-*Methylether*

To 250 g (1·76 moles) of stirred methyl iodide was added 41·8 g (0·176 mole) of silver dinitrocyanomethide over a 15 min period. The resulting mixture was stirred at room temperature for 1 hr and then diluted with an equal volume of ether. The solution was allowed to stand 1 hr and 39 g (94%) of silver iodide was collected on a funnel and washed with water to remove any unreacted silver dinitrocyanomethide. The ethereal filtrate was evaporated under reduced pressure to yield

14·9 g (58·3%) of yellow solid, m.p. 57–60°. This material was sufficiently pure for most purposes. A small portion of the product was recrystallized from water to yield a cream colored solid, m.p. 62–64°.

(Found: C, 24·51; H, 1·86; N, 28·70. Calc. for $C_3H_3N_3O_4$: C, 24·83; H, 2·08; N, 28·96.)

Solvolysis and Alkaline Decomposition of "Methyl Dinitroacetonitrile"

Samples of "methyl dinitroacetonitrile" were suspended in water which was heated to 50° and stirred while standard hydroxide solution was added continuously from a burette so as to maintain the pH of the solutions within the ranges indicated below; pH was determined with a Beckmann pH meter. The concentration of nitrite ion in the final solution was determined colorimetrically with Shinn reagent.[2] The concentration of dinitrocyanomethide ion was determined by measuring the extinction coefficient of the characteristic ultraviolet absorption band at 345 mμ. Formaldehyde was determined gravimetrically with methone. In experiments 6 and 7, the "methyl dinitroacetonitrile" was added to a 2·8-fold excess of potassium hydroxide dissolved in a mixture of equal volumes of ethylene glycol and isopropyl alcohol. After standing for 20 hr at 0° and 25°, respectively, the excess base was back-titrated. Nitrite ion was determined colorimetrically as above. Both solutions were examined for ultraviolet absorption at 345 mμ and from the absence of appreciable absorption it was concluded that dinitrocyanomethyl ion was not formed under these conditions.

TABLE 3. ALKALINE DEGRADATION OF "METHYL DINITROACETONITRILE"

Exp. no.	pH	Millimoles					Absorption max (mμ)
		Sample	Base	Nitrite	Dinitrocyano-methyl ion	HCHO	
1	6·5–7·0	2·496	1·96[a]	0·58	1·667	not measured	345
2	8–9	2·28	2·40[a]	0·383	[b]	0·189	335
3	8–9	2·07	3·52	1·32	0·617	0·617	345
4	6–7	1·38	1·36	0·440	0·820	0·130	345
5	6–7	1·38[c]	3·20	0·348	[b]	0·142	335–345
6	—	1·05	0·93	0·80	0·0	not measured	—
7	—	1·03	1·08	0·50	0·0	not measured	—

[a] Experiment terminated after 2–3 hr and complete reaction not assured.

[b] Concentration of dinitrocyanomethyl ion was made uncertain by extraneous absorption; the wavelength of ε_{max} was shifted.

[c] Methone (2·90 mmoles) added at beginning of the experiment.

Reaction of "Methyl Dinitroacetonitrile" with 2,4-Dinitrophenylhydrazine

A 2,4-dinitrophenylhydrazine reagent solution containing 2·7 g (0·014 mole) in a mixture of 70 ml of ethanol, 21 ml of water and 14 ml of sulfuric acid was prepared. "Methyl dinitroacetonitrile" (2·0 g, 0·014 mole) was added to this solution while it was stirred at room temperature. Complete dissolution took place as the temperature of the solution was raised to 50–55°, and maintained for thirty minutes. The solution was allowed to cool and stand for approximately sixty hours at room temperature. After cooling in an ice bath the mixture was filtered, giving 1·0 g (35% yield) of orange crystals, m.p. 158–159°. One recrystallization from ethanol raised the melting point to 161–162°. A mixture with authentic formaldehyde 2,4-dinitrophenylhydrazone (m.p. 162·5°–163·5°) melted at 161–163·5°.

Alkylation of dinitroacetonitrile with t-butyl alcohol; 2,2-dinitro-3,3-dimethylbutyronitrile and N-t- butyldinitroacetamide

The alkylation of dinitroacetonitrile with t-butyl alcohol to give 2,2-dinitro-3,3-dimethylbutyronitrile and N-t-butyl dinitroacetonitrile has been carried out under a variety of conditions. Dinitroacetonitrile both as the tetrahydrate and in the anhydrous form in solution was used. In some cases acetic acid and sulfuric acid were also introduced into the reaction media but their presence did not

[2] M. B. Shinn, *Industr. Engng. Chem.* (*Anal*). **13**, 33 (1941).

VOL. 17 1962

seem to be necessary. In an experiment where the reactants were dinitroacetonitrile in ether solution (prepared by acidification of the sodium salt with sulfuric acid), an additional mole of sulfuric acid and an excess of 2½ moles of t-butyl alcohol, a third, neutral, unidentified reaction product was also isolated. All three products were not isolated each time and the best yields of each were not obtained from any one experiment. As far as is known, all three products may be formed in every case, however.

A solution of 16·4 g (0·08 mole) of dinitroacetonitrile tetrahydrate and 12·4 g (0·08 mole) of sodium dinitrocyanomethide in 39·3 g (50 ml, 0·56 mole) of t-butyl alcohol was heated to 60° and stirred for 20 hr. A separate layer, presumably water saturated with sodium dinitrocyanomethide formed after 1 hr. The mixture was cooled, ether was added, and the lower layer was extracted with ether. Combined liquors and extracts were dried with magnesium sulfate before evaporating the solvent and excess t-butyl alcohol under reduced pressure. 2,2-Dinitro-3,3-dimethylbutyronitrile has a high vapor pressure and was speedily lost when evacuation was continued after solvent has been removed. The oily residue was extracted with petroleum ether which dissolved most of the 2,2-dinitro-3,3-dimethylbutyronitrile. Most of the N-t-butyldinitroacetamide remained in the oily residue. This residue was dissolved in ether and extracted with 5% sodium bicarbonate solution. Acidification of the bicarbonate extract with cold hydrochloric acid precipitated 1·2 g of solid material, m.p. 99–100°. The petroleum ether extract (above) was extracted with 5% sodium bicarbonate solution, and acidification of this bicarbonate extract gave another 0·3 g of solid material, m.p. 102–103°. These fractions were combined (1·5 g, 9·1%) and recrystallized from aqueous methanol several times; this raised the melting point to 110·5–111° (dec.).

(Found: C, 35·48; H, 4·70; N, 18·69; neut. equiv., 206·7. Calc. for $C_6H_{11}O_5N_3$(N-t-butyldinitroacetamide): C, 35·11; H, 5·40; N, 20·48; neut. equiv., 205.)

The petroleum ether extract (above) was concentrated at a low temperature. The concentrate when cooled to −70° gave white crystals which were recrystallized from aqueous ethanol, yield 2·1 g (13·6%) of product, m.p. 120° (dec). Successive recrystallizations from ethanol raised the melting point to 132–133° (dec.).

(Found: C, 38·75; H, 4·62; N, 21·84. Calc. for $C_6H_9O_4N_3$ (2,2-dinitro-3,3-dimethylbutyronitrile): C, 38·51; H, 4·85; N, 22·46.)

Isolation of the third product was carried out as follows: a suspension of 15·3 g (0·1 mole) of sodium dinitrocyanomethide in ether was treated with 10·2 g (0·1 mole) of sulfuric acid dropwise. After the sodium bisulfate was removed by filtration, the filtrate was added to 200 g (2·7 mole) of t-butyl alcohol, and 15 g (0·148 mole) of sulfuric acid was added to this solution. This mixture was kept at 50° for 24 hr. Removal of volatile material under reduced pressure left a heavy liquid which was extracted with two volumes of water to remove sulfuric acid and residual t-butyl alcohol, and was then dissolved in ether, washed twice with one-half volume of water and dried with magnesium sulfate. Evaporation of solvent left a solid residue which was washed onto a filter with 25% aqueous methanol. Yield of the residue was 11·0 g. This material was dissolved in warm benzene and N-t-butyl dinitroacetamide was precipitated by addition of petroleum ether. The filtrate was evaporated leaving a semi-solid residue. Addition of petroleum ether dissolved away 2,2-dinitro-3,3-dimethylbutyronitrile and left a solid, m.p. 162–165°, yield 1·3 g. Successive recrystallizations from aqueous methanol raised the melting point to 164–165°.

(Found: C, 50·90; H, 6·82; N, 25·43; mol. wt. (ebull., acetone), 268.)

Alkylation of Silver Dinitrocyanomethide with t-Butyl Bromide

To 55·0 g (0·40 mole) of t-butyl bromide immersed in a cooling bath was added with stirring 9·6 g (0·04 mole) of silver dinitrocyanomethide. The resulting mixture was stirred at room temperature for 2 hr and then diluted with 200 ml of ether. After standing overnight, 7·3 g (97%) of silver bromide was collected on a funnel and then washed with acetone to remove any unreacted silver dinitrocyanomethide. The ethereal filtrate was evaporated under reduced pressure to yield 9·1 g of a yellow oil, a mixture of 2,2-dinitro-3,3-dimethylbutyronitrile and N-t-butyldinitroacetamide. Separation of the mixture of nitrogen and carbon alkylated products was affected by dissolving the crude material in 250 ml portions of 5% sodium hydroxide. Evaporation of the ether under reduced pressure gave an oil, the absorption spectrum of which was identical to that of the previously prepared 2,2-dinitro-3,3-dimethylbutyronitrile. Sublimation of the oil at 60–70°/20 mm gave 1·3 g (17%) of a white, waxy

solid (m.p. 120–124°) having a strong camphor-like odor. Infrared examination showed a dinitrocyanomethyl absorption band at 1595 cm^{-1}. The sample volatilized before elemental analyses were obtained. Acidification of the basic extract with dilute sulfuric acid liberated the amide which was crystallized from warm aqueous methanol to give 1·5 g (18%) of N-t-butyldinitroacetamide, m.p. 110–111° dec.

(Found: C, 35·42; H, 5·32; N, 20·93; neut. equiv. 204·0. Calc. for $C_6H_{11}O_5N_3$: C, 35·12; H, 5·41; N, 20·48; neut. equiv., 205·2.)

Methyl 4,4-*Dinitro*-4-*Cyanobutyrate*

A mixture of 24·0 g (0·128 mole) of dinitroacetonitrile tetrahydrate and 17·2 g (0·2 mole) of methyl acrylate in 35 ml of methanol was heated at 50° for 5 hr. During this period the solution became very dark. After standing overnight, volatile material was removed under reduced pressure. The liquid residue was dissolved in ether, washed with 5% bicarbonate solution and with water, and then dried over anhydrous magnesium sulfate. When the solvent was removed there remained 8·4 g of crude liquid. This material was flash distilled from a bath at 100–120°/0·05 mm yielding 5·8 g (21%) of pale yellow distillate. The infrared spectrum of this material showed a carbonyl ester band at 1739 cm^{-1}, the dinitrocyanomethyl band at 1600 cm^{-1}, and a weak cyano band at 2250 cm^{-1}. A portion of the product was redistilled. The entire sample came over at 78–80°/0·12–0·15 mm, n_D^{β} 1·4595.

(Found: C, 33·40; H, 2·28; N, 19·55. Calc. for $C_5H_5O_6N_3$: C, 33·18; H, 3·23; N, 19·35.)

Acid Hydrolysis of Methyl 4,4-*Dinitro*-4-*Cyanobutyrate to Succinic Acid*

A mixture of 1·2 g (0·0055 mole) of methyl 4,4-dinitro-4-cyanobutyrate and 15 ml of 20% hydrochloric acid was heated under reflux for 3 hr. When the mixture was cooled, a brown solid crystallized, yield 0·5 g (91%). Treatment with carbon during recrystallization from water yielded white crystals, m.p. 186–189°, neut. equiv. 60·5 (succinic acid, m.p. 188°, neut. equiv. 59). The infrared spectrum of this material showed it to be a dicarboxylic acid without any absorption bands attributable to ester, nitro, or nitrile groups.

4,4-*Dinitro*-4-*Cyanobutyramide*

A suspension of 12·5 g (0·08 mole) of sodium dinitrocyanomethide in 250 ml of ether was acidified by the dropwise addition of 4·2 g (0·041 mole) of sulfuric acid at room temperature. This suspension was stirred for 30 min and was then filtered to remove sodium sulfate. Recrystallized acrylamide, 5·8 g (0·08 mole) was dissolved in the ether filtrate with the addition of a little ethyl acetate to facilitate solution. The solution then was heated under reflux for 24 hr. About 0·5 g of insoluble material was removed by filtration. Solvent was evaporated from the filtrate leaving 12 g of partially crystalline residue. After addition of methylene chloride, 7·0 g of crystalline product was obtained. This was dissolved in ethanol and filtered to remove insoluble material. Benzene was added to the alcohol solution which was concentrated, yielding 5·9 g (29·0%) of crystalline material, m.p. 43–5°. After three recrystallizations from a chloroform-ethanol mixture, the product melted at 62–63°.

(Found: C, 29·96; H, 2·53; N, 27·58. Calc. for $C_5H_6O_4N_4$: C, 29·71; H, 2·99; N, 27·72.)

4,4-*Dinitro*-4-*Carbamylbutyric Acid and* 4,4-*Dinitro*-4-*Cyanobutyric Acid*

A solution of 14·5 g (0·204 mole) of glacial acrylic acid and 28·5 g (0·14 mole) of dinitroacetonitrile tetrahydrate in 15 ml of water was allowed to stand 48 hr at 25–35°. When volatile material had been evaporated under reduced pressure, there remained 29·6 g of crystalline solid, m.p. 95–112°. Recrystallization from a mixture of equal parts by volume of chloroform and benzene yielded 18·5 g (60%) of 4,4-dinitro-4-carbamylbutyric acid, m.p. 104–109°. After one recrystallization from an ether-chloroform mixture in the presence of the decolorizing carbon, three additional recrystallizations from the same solvent gave a colorless product which melted at 115–117°.

(Found: C, 27·45; H, 3·08; N, 19·24; neut. equiv., 74·8. Calc. for $C_5H_7O_7N_3$: C, 27·16; H, 3·17; N, 19·00; neut. equiv., 73·7.)

The filtrate from the first crystallization (chloroform–benzene solution) was evaporated, and after a second small crop of the above material was removed, the residue consisted of 3·7 g (13%) of 4,4-dinitro-4-cyanobutyric acid, m.p. 72–74°. After several recrystallizations from chloroform the product melted at 73–74°.

(Found: C, 29·34; H, 2·34; N, 20·39; neut. equiv., 68·6. Calc. for $C_5H_5O_4N_3$: C, 29·57; H, 2·48; N, 20·69; neut. equiv., 67·7.)

VOL. 17 1962

4,4-Dinitro-4-Carbamylbutyric Acid

To a solution of 4·0 g (0·056 mole) of acrylic acid in 11 ml of t-butyl alcohol was added 8·0 g (0·039 mole) of dinitroacetonitrile tetrahydrate. After the solution had been allowed to stand for 14 hr, solvent was evaporated under reduced pressure. The residue was triturated with chloroform and filtered, yielding 6·0 g (69%) of solid, m.p. 111–113°. No depression in melting point was observed during a mixed melting point with material prepared above (m.p. 115–117°). There appeared to be some of the normal (cyano-) adduct present in the chloroform filtrate, but this could not be purified readily.

α,α-Dinitroglutarimide

A solution of 10·0 g (0·065 mole) of sodium dinitrocyanomethide in 80 ml of ethyl acetate was acidified by the dropwise addition of 3·3 g (0·033 mole) of sulfuric acid at room temperature. After stirring for 30 min the mixture was filtered and 5·0 g (0·07 mole) of glacial acrylic acid was added to the filtrate. The reaction was allowed to proceed for 12 hr at 40°. Solvent was removed under reduced pressure leaving 15 g of residue. Extraction of the residue with ether and chloroform yielded 4·5 g (34%) of α,α-dinitro-glutarimide, m.p. 141–143°. Recrystallization, once from water and twice from an ethyl acetate–cyclohexane mixture, yielded α,α-dinitro-glutarimide which melted at 146–148°. The product was slightly acid. Its infrared spectrum did not have a nitrile absorption band and made the presence of a carboxyl group doubtful. The absorption band at 1578 cm^{-1} suggested the possibility of a dinitrocyanomethyl group. The infrared spectrum showed NH bands at 3160 and 3060 cm^{-1}; the presence of the second band is presumably due to the presence of some impurity, possibly the uncyclized product.

(Found: C, 30·07; H, 2·54; N, 20·96. Calc. for $C_5H_5O_6N_3$: C, 29·57; H, 2·48; N, 20·69.)

Dehydration 4,4-Dinitro-4-Carbamylbutyric Acid to α,α-Dinitroglutarimide

A solution of 0·7 g (0·0032 mole) of 4,4-dinitro-4-carbamylbutyric acid, m.p. 115–117° in 30 ml of acetonitrile was treated with an excess of phosphorus pentoxide, and an exothermic reaction was observed. The mixture was stirred for 2 hr and then evaporated to dryness. The residue was extracted with ether. The ether extracts were evaporated leaving 0·3 g (46%) of material which melted at 148—150°. After recrystallization from a mixture of ethyl acetate and chloroform, the product melted at 150–151°. A mixture melting point with a sample prepared by the Michael addition reaction in t-butyl alcohol solution gave no depression, and the infrared spectra of both products were identical.

4,4-Dinitro-4-Cyanobutyraldehyde Dimethylacetal

Dinitroacetonitrile tetrahydrate, 9·2 g (0·045 mole), was added to a solution of 2·8 g (0·05 mole) of acrolein in 10 ml of water. After the solution had been allowed to stand for 40 hr, the amount of oil which had formed a lower layer was 8·0 g (96%). The oily layer was separated, dissolved in 30 ml of methanol, treated with 9·4 g (0·089 mole) of methyl orthoformate and 0·08 g of *p*-toluenesulfonic acid monohydrate and heated under reflux for 5 hr. All volatile material was removed under reduced pressure, leaving 6·6 g (66%) of yellow liquid which was distilled. The fraction which distilled at 80–81°/0·4 mm weighed 5·7 g (57%).

(Found: C, 35·83; H, 4·51; N, 18·68. Calc. for $C_7H_{11}O_6N_3$: C, 36·05; H, 4·75; N, 18·01.)

The crude adduct from another reaction was flash distilled instead of converting it to the acetal. Material which distilled at 90–100°/1·0–0·55 mm amounted to 3·6 g (31%). During redistillation at 80–92°/0·75–1·3 mm, partial decomposition could not be avoided, and the product which was obtained was not of satisfactory purity.

(Found: C, 36·13; H, 2·80; N, 19·34. Calc. for $C_5H_5O_5N_3$: C, 32·11; H, 2·69; N, 22·46.)

1,3,5-Tris-(γ,γ-Dinitro-γ-Cyanobutyryl)Perhydro-s-Triazine

Dinitroacetonitrile tetrahydrate, 9·0 g (0·044 mole) was added to a solution of 4·0 g (0·016 mole) of recrystallized 1,3,5-tri-acrylylperhydro-s-triazine in 250 ml of methanol, and the solution was stirred at 35–40° for 15 hr. Solvent was evaporated under reduced pressure leaving a mixture of oil and crystals. When this material was dissolved in ethanol, addition of chloroform caused crystallization of 2·5 g (26%) of product, m.p. 143–145°. This was recrystallized again from ethanol–chloroform without changing the melting point.

(Found: C, 34·14; H, 3·03; N, 26·09. Calc. for $C_{18}H_{18}O_{15}N_{12}$: C, 33·66; H, 2·82; N, 26·17.)

Methylene-Bis-4,4-Dinitro-4-Cyanobutyramide

Dinitroacetonitrile tetrahydrate, 25·0 g (0·123 mole), was added to a solution of 10·0 g (0·065 mole) of recrystallized methylene-bis-acrylamide in 300 ml of water and the solution was stirred at 55° for 7 hr. Most of the solvent was removed under reduced pressure. The residue was dissolved in a little alcohol and crystallized after the addition of water to yield 8·0 g (31%) of product, m.p. 134–135°. After several recrystallizations from aqueous ethanol, the melting point was unchanged.

(Found: C, 32·15; H, 2·62; N, 27·80. Calc. for $C_{11}H_{12}O_{10}N_6$: C, 31·73; H, 2·91; N, 26·92.)

5,5-Dinitro-5-Cyanopentanone-2

Addition of 5·0 g (0·07 mole) of methylvinyl ketone to a solution of 12·0 g (0·059 mole) of dinitroacetonitrile tetrahydrate in 15 ml of water was accompanied by slight evolution of heat. Separation of the solution into two layers took place within a few minutes. After the reaction mixture had been allowed to stand at room temperature for five days (this time was probably longer than necessary), the layers were separated. The oily layer weighed 11·0 g, 92·5% crude yield. It was washed three times with 35 ml portions of water, dissolved in ether and dried with magnesium sulfate. After removal of drying agent and solvent, the residue was flash distilled from a bath at 100–104°/0·5–1·0 mm, giving 8·1 g (68% yield) of distillate, n_D^{25} 1·4650. Redistillation in conventional apparatus proved unsatisfactory because a steady pressure could not be maintained. The product was redistilled through a falling-film still at 77°/0·2–0·5 mm giving a distillate with n_D^{25} 1·4646.

(Found: C, 36·62; H, 3·22; N, 20·53. Calc. for $C_8H_7O_6N_3$: C, 35·82; H, 3·51; N, 20·89.)

From the distillate a semicarbazone derivative was prepared by standard procedures. After several recrystallizations from aqueous ethanol, the derivative melted at 137–138° (dec.).

(Found: C, 32·67; H, 3·86; N, 32·43. Calc. for $C_7H_{10}O_5N_6$: C, 32·56; H, 3·88; N, 32·56.)

The infrared spectrum of the ketone contained absorption bands attributed to the following functional groups: nitrile at 2245 cm^{-1}, ketone carbonyl at 1721 cm^{-1} and dinitrocyanomethyl at 1599 and 1297 cm^{-1}.

Mannich Type Reaction Products of Dinitroacetonitrile

These compounds have all been prepared successfully by the same general procedure, which is the best procedure developed thus far but does not represent the result of an intensive search for optimum conditions. In every case dinitroacetonitrile was used as obtained by neutralizing sodium dinitrocyanomethide in ethyl acetate solution with one equivalent of sulfuric acid. After stirring the mixture for 30 min, the sodium sulfate was removed by filtration and the filtrate was used as indicated.

N-(2,2-Dinitro-2-Cyanoethyl)Benzamide

A solution of 5·0 g (0·033 mole) of N-methylolbenzamide[3] in 30 ml of ethyl acetate was stirred and heated to 50°. A solution of dinitroacetonitrile (0·033 mole) in 50 ml of ethyl acetate was added to it dropwise over a period of 2 hr. The reaction mixture was maintained at a temperature of 50° for an additional 30 min and cooled. All volatile material was removed by evaporation under reduced pressure. The viscous residue was extracted with methylene chloride and filtered to remove methylene-bis-benzamide. When the solvent was again evaporated, the residue crystallized. It was washed onto a filter with cold water containing a little ethanol and dried. The weight of crude product amounted to 1·7 g (20%), m.p. 117–118°. After recrystallization once from carbon tetrachloride and twice from benzene, the melting point increased to 119·5–120·5°.

(Found: C, 46·15; H, 2·40; N, 22·82. Calc. for $C_{10}H_8O_5N_4$: C, 45·46; H, 3·03; N, 21·21.)

N-(2,2-Dinitro-2-Cyanoethyl)Acetamide

A solution of 8·1 g (0·09 mole) of N-methylolacetamide[4] in 30 ml of ethyl acetate was stirred at room temperature and treated with a solution of dinitroacetonitrile (0·09 mole) in 50 ml of ethyl acetate. About 5 g of anhydrous magnesium sulfate was added to the solution which was warmed to 30° and allowed to stand for 2 hr. The solution was filtered and all volatile material evaporated from the filtrate under reduced pressure. The viscous residue was shaken once with two to three volumes of ice water which was immediately decanted. The residue was dissolved in ether and dried with magnesium sulfate. After the mixture had been filtered again and solvent evaporated from the filtrate, the

[3] A. Einhorn, *Liebigs Ann.* **343,** 207 (1905).
[4] A. Chwala, *Chem. Abstr.* **43,** 569 (1949).

residue crystallized when it was chilled. The weight of product was 5·5 g (33%) m.p. 70–73°. It was recrystallized from benzene to a constant melting point of 76·5–77·5°.

(Found: C, 29·47; H, 3·10; N, 27·51. Calc. for $C_5H_6O_5N_4$: C, 29·70; H, 2·97; N, 27·72.)

N-(2,2-*Dinitro*-2-*Cyanoethyl*) *Methacrylamide*

A mixture of 4·25 g (0·05 mole) of methacrylamide and 1·5 g (0·05 mole) of paraformaldehyde was ground together in a mortar. Two drops of nearly saturated aqueous potassium carbonate solution was added to the mixture and grinding was continued for 2–3 min. The mixture was scraped into a test tube and heated to 50–60° with stirring; it gradually melted to give a clear liquid. This was cooled, dissolved in 40 ml of dioxane and filtered. The solution was stirred while 14 g of pulverized Drierite was added to it. The suspension was heated to 40–45° and stirred while a solution of dinitroacetonitrile (0·05 mole) in 50 ml of ethyl acetate was added dropwise during a period of 2 hr. Heating at 40–45° was continued for 30 min. The mixture was cooled, filtered, and all volatile material evaporated from the filtrate under reduced pressure. The viscous residue was covered with one to two volumes of ice water, a few drops of ethanol were added and the mixture was triturated. The solid product, when filtered and dried, weighed 3·3 g (27%), m.p. 70–73°. After two recrystallizations from benzene the product melted at 74–75°.

(Found: C, 36·54; H, 2·78; N, 24·15. Calc. for $C_7H_8O_5N_4$: C, 36·84; H, 3·51; N, 24·56.)

N-(2,2-*Dinitro*-2-*Cyanoethyl*)*Acrylamide*

This preparation was carried out in exactly the same manner as the preceding one, using the same molar quantities of the analogous reagents. When all volatile material had been removed from the reaction mixture and the viscous residue was triturated with ice-water and a little ethanol, crystallization did not take place. The oily product was dissolved in ether, dried with magnesium sulfate, and the ether evaporated again. Addition of carbon tetrachloride and a little ether brought about crystallization after trituration in an ice-bath. The dried product weighed 2·1 g (20%), m.p. 80–82°. After two recrystallizations from benzene the melting point was 77–78°.

(Found: C, 34·14; H, 2·79; N, 26·44. Calc. for $C_6H_6O_5N_4$: C, 33·64; H, 2·80; N, 25·17.)

N,N′-*Bis*-(2,2-*Dinitro*-2-*Cyanoethyl*)*Urea*

Dimethylolurea, 13·2 g (0·11 mole) and anhydrous magnesium sulfate, 9·0 g (0·075 mole), were suspended in 100 ml of ethyl acetate and stirred at 12° for 5 hr while a solution of dinitroacetonitrile (0·22 mole) in ethyl acetate was added dropwise. Stirring at 12° was continued overnight and for 5 hr at room temperature the following day. Suspended solids were filtered and the volatile material was evaporated from the filtrate under reduced pressure. When the viscous residue was triturated with cold water, it solidified and was filtered and dried. It was extracted thoroughly with ethyl ether and filtered. The residual solid appeared to be polymeric. Evaporation of the ether left 1·5 g (4%) of solid which melted at 127°. Extraction of this material with boiling ethylene dichloride dissolved only a trace of product which crystallized from the filtrate when cooled, m.p. 128°. The bulk of material which remained undissolved was extracted with boiling trichloroethane and filtered. Most of the solid again remained undissolved and crystals obtained from the filtrate melted at 134°. The residue was finally dissolved in ether; the solution was cooled in an ice bath and product was crystallized by gradual addition of petroleum ether. This material melted at 136°, and analytical data reported for this compound were obtained from this sample.

(Found: C, 24·71; H, 2·52; N, 32·01. Calc. for $C_7H_8O_9N_8$: C, 24·28; H, 1·73; N, 32·37.)

2,2-*Dinitro*-2-*Cyanoethanol*

Seventy-six and one half grams of sodium dinitrocyanomethide (0·5 mole) was dissolved in small portions at room temperature in 250 ml of 37% formalin. Twenty-seven and eight-tenths milliliters of chilled concentrated sulfuric acid (0·5 mole) was added with stirring over a ½ hr period. The reaction temperature was maintained between 23 and 26° during this time by means of an ice bath. The reaction mixture was allowed to stand at room temperature for four days and was then extracted with four 50 ml portions of ether. The ether extracts were combined and dried over anhydrous magnesium sulfate. The ether was removed *in vacuo* to yield 76·5 g of 2,2-dinitro-2-cyanoethanol (95% yield). The product was a light yellow liquid, n_D^{20} 1·4470, which solidified on standing overnight in the refrigerator.

VOL. 17 1962

2,2-Dinitro-2-Cyanoethyl Methacrylate

To 23·8 g (0·113 mole) of trifluoroacetic anhydride and 1·0 g of di-β-naphthol was added dropwise with cooling 9·7 g (0·113 mole) of anhydrous methacrylic acid at such a rate that the temperature did not exceed 30°. The mixture was stirred mechanically at room temperature for 5 min and then 14·0 g (0·087 mole) of 2,2-dinitro-2-cyanoethanol was added dropwise at a temperature of 20–30°. The reaction mixture was stirred for 1 hr and was then poured into 500 ml of ice water. The aqueous mixture was first extracted with a total of 200 ml of ether, and the ether and water layers were then neutralized by the addition of solid sodium bicarbonate. The ether layer was separated and the aqueous layer was extracted with two 50 ml portions of ether. The combined ethereal solution was washed with 50 ml of water and dried over magnesium sulfate. The solvent was removed under reduced pressure to give 15·7 g (79%) of crude ester, which contained a trace of trifluoroacetate as was indicated by its infrared spectrum. The material was flash distilled to yield 6·4 g (32%) of 2,2-dinitro-2-cyanoethyl methacrylate, b.p. 53–58°/0·07 mm. The spectrum of the distillate showed a nitrile absorption band at 2260 cm^{-1}, an ester band at 1740 cm^{-1}, and a dinitrocyanomethyl band at 1602 cm^{-1}.

(Found: C, 36·80; H, 2·91; neut. equiv., 113·5. Calc. for $C_7H_7O_6N_3$: C, 36·69; H, 3·08; neut. equiv., 114·5).

2,2-Dinitro-2-Cyanoethyl Acetate

The procedure described above was used with 27·3 g (0·13 mole) of trifluoracetic anhydride, 7·8 g (0·13 mole) of acetic acid, and 16·0 g (0·10 mole) of 2,2-dinitro-2-cyanoethanol to give 11·3 g (57%) of crude 2,2-dinitro-2-cyanoethyl acetate. Vacuum distillation gave 6·9 g (34%) of product, b.p. 71–92°/1·0 mm. Another fractionation of this material gave 5·2 g (26%) of pure, 2,2-dinitro-2-cyanoethyl acetate, b.p. 73–75°/1·25 mm n_D^{20} 1·4439, d_4^{20} 1·335.

(Found: C, 30·97; H, 2·45; N, 20·99. Calc. for $C_5H_5O_6N_3$: C, 29·57; H, 2·48; N, 20·69.)

2,2-Dinitro-2-Cyanoethyl Acrylate

To 50 ml of chloroform was added 3·5 g (0·022 mole) of 2,2-dinitro-2-cyanoethanol, 1·3 g (0·010 mole) of aluminum chloride, and approximately 1·0 g of p-hydroxydiphenylamine. The mixture was stirred mechanically while 1·8 g (0·020 mole) of acrylyl chloride was added with cooling at a temperature of 24–27°. Fifteen minutes after all the acid chloride was added there was no evidence of evolution of hydrogen chloride. The reaction mixture was then heated to 30–35° for 1 hr, and the temperature was increased to 35–40° for an additional hour. After 2 hr of heating rapid evolution of hydrogen chloride had ceased. The mixture was cooled to room temperature, poured into 500 ml of ice water, the chloroform layer separated, and the aqueous layer extracted with three 100 ml portions of chloroform. The chloroform extracts were filtered to remove any aluminum chloride present, and the filtrate was washed with 1% sodium bicarbonate to remove any unreacted acrylyl chloride. After drying the chloroform solution over magnesium sulfate and evaporation of the solvent under reduced pressure, there was obtained 3·2 g (74%) of crude product. Distillation of the material yielded 2·1 g (49%) of ester, b.p. 56–60°/0·1 mm. The distillate, on infrared examination, exhibited a carbonyl absorption band at 1750 cm^{-1} and the expected dinitro-cyanomethyl band at 1600 cm^{-1}.

(Found: C, 32·78; H, 2·21; N, 19·42. Calc. for $C_6H_5O_6N_3$: C, 33·50; H, 2·34; N, 19·53.)

Nitration of 2,2-Dinitro-2-Cyanoethanol

To 105 g of mixed acid (42 g of concentrated nitric acid and 63 g of concentrated sulfuric acid) there was added dropwise 12·0 g (0·075 mole) of 2,2-dinitro-2-cyanoethanol at a temperature of 0–5°. After addition of the alcohol, the reaction mixture was removed from the ice-salt bath and allowed to warm to 10°. Oily droplets began to form on the surface of the mixture, which was then poured into 500 ml of ice water. The oily layer was extracted with one 300 ml and two 50 ml portions of ether. The ethereal solution was washed with 50 ml of 1% sodium bicarbonate and three 50 ml portions of water. The ether solution was dried over magnesium sulfate, and the solvent was evaporated under reduced pressure to give 10·3 g (67%) of crude product. A portion of the crude liquid was distilled at reduced pressure to give a colorless liquid, b.p. 46–55°/0·1 mm. The infrared spectrum of this material showed an intense dinitrocyanomethyl band at 1600 cm^{-1} and an intense nitrate ester band at 1678 cm^{-1}.

(Found: N, 24·62. Calc. for $C_3H_2O_7N_4$: N, 27·19.)

VOL. 17 1962

2,2-Dinitro-2-Cyanoethyl Trifluoroacetate

When 2,2-dinitro-2-cyanoethanol (above) was added to 25 g of trifluoracetic anhydride at 0–5°, the alcohol did not dissolve. The anhydride was heated to reflux and addition of 2,2-dinitro-2-cyanoethanol was continued. The alcohol slowly dissolved under these conditions. The mixture was heated at 55° for another hour and allowed to stand overnight. All volatile material was removed under reduced pressure. The residue was treated with 0·2 g of ethyl centralite and distilled. Three fractions were obtained: (1) 11·3 g, b.p. 33–38°/0·04–0·06 mm, n_D^{20} 1·4037; (2) 1·6 g, 32–39°/0·05–0·08 mm, n_D^{20} 1·4045; (3) 1·9 g, b.p. 80°/0·20–0·24 mm. Fractions 1 and 2 were combined and redistilled yielding a constant boiling fraction, 11·2 g, b.p. 39°/0·15 mm, n_D^{20} 1·4045. The overall yield based on sodium dinitrocyanomethide was 36·6%. The infrared spectrum of this material contained a band at 1812 cm^{-1} attributed to the trifluoroacetyl group, the dinitrocyanomethyl band at 1610 cm^{-1}, and a very weak cyano band at 2260 cm^{-1}.

(Found: C, 23·31; H, 0·53; N, 15·97; sapn. equiv., 129·8. Calc. for $C_5H_2O_6N_3F_3$: C, 23·35; H, 0·78; N, 16·34; sapn. equiv., 128·5.)

2,2-Dinitro-2-Cyanoethyl Methacrylate

To 1000 ml of chloroform was added 42·0 g (0·261 mole) of 2,2-dinitro-2-cyanoethanol, 53·5 g (0·40 mole) of aluminum chloride, and 1·5 g of cuprous chloride. The mixture was stirred mechanically while 25·1 g (0·240 mole) of methacrylyl chloride was added with cooling at a temperature of 18–23°. There was no evidence of the evolution of hydrogen chloride. The reaction mixture was heated to 50–60° for 5 hr, then an additional quantity of inhibitor was added before heating seven hours at the same temperature. The mixture was cooled to room temperature, filtered into 2400 ml of ice water, the chloroform layer separated, and the aqueous layer extracted with four 150 ml portions of chloroform. The combined chloroform extract was washed with four 100 ml portions of 5% sodium bicarbonate to remove any unreacted methacrylyl chloride. After drying the chloroform solution over anhydrous magnesium sulfate and evaporating the solvent under reduced pressure, there was obtained 24·2 g (97%) of crude ester. Flash distillation of the crude product yielded 12·9 g (51%), b.p. 62–64°/0·17 mm, n_D^{20} 1·4573.

(Found: C, 37·25; H, 3·32; N, 16·49. Calc. for $C_7H_7O_6N_3$: C, 36·69; H, 3·08; N, 18·34.)

The distillate was flash distilled again to give 11·7 g (47%) of 2,2-dinitro-2-cyanoethyl methacrylate, b.p. 59–62°/0·07–0·10 mm, n_D^{20} 1·4582 and d_4^{20} 1·174. The spectrum was in agreement with that of the previously reported methacrylate prepared via the mixed anhydride technique.

(Found: C, 36·81; H, 3·98; N, 18·63. Calc. for $C_7H_7O_6N_3$: C, 36·69; H, 3·08; N, 18·34.)

Reaction of 2,2-Dinitro-2-Cyanoethanol with Sulfuric Acid and Trioxane

Dinitrocyanoethanol (16·1 g, 0·1 mole) was added dropwise to 50 g of sulfuric acid while the solution was stirred and cooled to maintain the reaction temperature below 60°. When this addition was finished, 3·0 g (0·1 mole) of trioxane was added portionwise to the reaction mixture. After a few minutes of stirring, a white precipitate formed. The reaction mixture was stirred until it cooled to room temperature, was allowed to stand overnight, and was poured onto 150 g of crushed ice; the product was collected on a filter and was washed with water and ethanol. The weight of dried product was 12·5 g. When heated a sample darkened at 180° and decomposed at 220–225°.

The product was insoluble in hot water, hot ethanol, and ether. It was quite soluble in acetone and ethyl acetate. Samples were recrystallized from acetic acid (m.p. 222° dec.), acetonitrile (m.p. 223° dec.), and acetone–ethanol (m.p. 223° dec.). A sample recrystallized twice from acetone–ethanol m.p. 224–225° dec., was analyzed.

(Found: C, 28·05; H, 2·88; N, 25·51; M. W., 364. C, 29·45; H, 3·54; N, 21·65.* Calc. for $C_9H_{10}O_{12}N_6$: C, 27·41; H, 2·54; N, 21·32; M. W., 394.)

Alkaline Degradation of Dinitroacetonitrile Derivatives

Reaction of methyl 4,4-dinitro-4-cyanobutyrate with potassium hydroxide

To 1·28 g (0·023 mole) of potassium hydroxide in 15 ml of anhydrous methanol was added dropwise 2·5 g (0·0115 mole) of methyl 4,4-dinitro-4-cyanobutyrate. The resulting 12° rise in temperature was accompanied by immediate precipitation of a yellow material. One hour later there was

* Different preparation; sample recrystallized twice from acetonitrile, mp. 225° dec.

collected on a filter 1·9 g of bright yellow solid which after two recrystallizations from hot methanol melted at 160–161°; on the basis of elemental analysis it appeared to be the potassium salt of methyl 4,4-dinitrobutyrate.

(Found: C, 26·98; H, 3.46; N, 13·16; K, 16·98. Calc. for $C_5H_7O_6N_2K$: C, 26·08; H, 3·06; N, 12·17; K, 16·98.)

Methyl 4,4-Dinitrobutyrate

Eleven and one-half grams (0·05 mole) of the potassium salt of methyl 4,4-dinitrobutyrate (obtained from the alkaline degradation of methyl 4-cyano-4,4-dinitrobutyrate) dissolved in 300 ml of distilled water was neutralized with sulfuric acid. Potassium sulfate was formed immediately and a yellow oil separated as the neutralization proceeded. When the aqueous mixture was definitely acidic, the white precipitate of potassium sulfate had gone back into solution and the oily product had settled to the bottom of the container. One hour later the yellow oil was separated and the aqueous layer was extracted with six 200 ml portions of ether. After addition of the original oily layer to the combined ether extracts, the resulting ethereal solution was washed with five 100 ml portions of distilled water and dried over anhydrous magnesium sulfate. Removal of the drying agent and subsequent evaporation of the solvent under reduced pressure yielded 5·4 g (67%) of crude products. Distillation of a portion of the crude material gave 1·5 g of clear liquid, b.p. 50–51°/0·07 mm, n_D^{20} 1·4542. Infrared spectra of the crude product and the distillate were identical, and the elemental analysis, although a little high for carbon and nitrogen, indicated that the material was methyl 4,4-dinitrobutyrate.

(Found: C, 32·34; H, 4·40; N, 15·34. Calc. for $C_5H_8O_6N_2$: C, 31·25; H, 4·20; N, 14·58.)

The remaining portion of the crude product (approximately 3·9 g) was purified by distillation through a bulb still, head temperature 55–57°/0·04 mm, pot temperature 84–86°, to yield 1·8 g, n_D^{20} 1·4550. Redistillation of this sample through the same apparatus, pot temperature 84–86° head temperature 46–47°/0·03 mm, gave 1·0 g, n_D^{20} 1·4554. The infrared spectrum of this final distillate was identical with that of the first, and elemental analyses were not made. The molecular weight was determined.

(Found: M. W., 200·3, 201·7. Calc. for $C_5H_8O_6N_2$: M. W., 192·1.)

Reaction of the Sodium Salt of Methyl 4,4-Dinitrobutyrate with Methyl Acrylate

To 4·28 g (0·02 mole) of sodium salt (obtained from reaction of methyl 4,4-dinitro-4-cyanobutyrate with sodium methylate) in 10 ml of distilled water was added 1·70 g (0·0197 mole) of methyl acrylate at 27–31°. The reaction mixture immediately turned dark and a flocculent precipitate separated. After 24 hr the oil which had formed was extracted with four 50 ml portions of ether and the combined ether extract was dried over anhydrous magnesium sulfate. Removal of the drying agent and complete evaporation of the ether under reduced pressure gave 2·4 g of an almost white solid, m.p. 43–45°. When the crude material was dissolved in a minimum of hot ethanol, treated with decolorizing charcoal, filtered, and chilled, there was obtained 2·2 g (40%) of snow-white dimethyl 4,4-dinitropimelate, m.p. 45·5–46·0°.

Tetrahedron, 1962, Vol. 17, pp. 105 to 106. Pergamon Press, Ltd. Printed in Northern Ireland

CHEMISTRY OF DINITROACETONITRILE—III

DINITROACETAMIDE AND ITS DERIVATIVES

CHARLES O. PARKER
Rohm & Haas Co., Redstone Arsenal Research Division
Huntsville, Alabama

VOL. 17 1962

(*Received* 23 *March* 1961)

Abstract—Dinitroacetamide was prepared by acid hydrolysis of dinitrocyanomethide salts. Manipulation of preparative quantities of dinitroacetamide or its salts was troublesome due to unfavorable solubility properties and relatively facile decomposition to give dinitromethane derivatives. Dinitroacetamide underwent normal Michael addition reactions and condensed with formaldehyde to give 2,2-dinitro-2-carbamylethanol of which acetate ester and N-acylamido-derivatives were prepared.

THE chemistry of dinitroacetamide has been briefly surveyed. Factors affecting the yield of product and occurrence of by-products were investigated at some length but from an empirical approach since the mechanics of the preparative reaction were never well understood. The chemical properties of dinitroacetamide have been shown to be typical of a geminal dinitrocompound, modified by the general tendency of dinitroacetamide, its salts and derivatives to undergo rather facile hydrolysis of the carbamyl group giving derivatives of dinitromethane. Except for this tendency dinitroacetamide formed salts and gave derivatives having the expected properties in reactions with formaldehyde and with carbonyl-conjugated unsaturated compounds. The Michael adduct of dinitroacetamide with acrylic acid was shown to be identical with the product isolated from the analogous reaction with dinitroacetonitrile tetrahydrate.[1]

Dinitroacetamide was prepared by treatment of solutions of dried sodium, ammonium or potassium dinitrocyanomethide salts in methanol–ethyl acetate solution with gaseous hydrogen chloride. Product was isolated from such reaction mixtures simply by evaporation of all volatile material, i.e. without recourse to any intentional hydrolysis treatment. Some conversion to dinitroacetamide could be effected using methanol or ethanol alone or mixed with ether instead of ethyl acetate; even from concentrated aqueous hydrochloric acid an impure dinitroacetamide could be obtained.

The optimum conditions for the preparative reaction comprised use of approximately the minimum amount of methanol–ethyl acetate solution required for dissolution of the dinitrocyanomethide salt. Greater amounts of alcohol gave increasing quantities of side reaction products, mainly the dinitroacetate ester but also dinitromethane. Separation of dinitroacetamide from crude mixtures containing these compounds as impurities by recrystallization of the dinitroacetamide or its potassium salt was found to be inefficient and wasteful. The dinitroacetamide salt was the most soluble of the three.

The effect of concentrated acids on the hydrolysis of sodium dinitrocyanomethide has been investigated by spectrophotometric means. Concentrated sulfuric, 85 per cent phosphoric, and concentrated hydrochloric acids have been used. Only in the

[1] Part II: C. O. Parker, W. D. Emmons, A. S. Pagano, H. A. Rolewicz and K. S. McCallum, *Tetrahedron* **17**, 89 (1962).

case of concentrated hydrochloric acid however, have the results been sufficiently clear-cut to enable definite conclusions to be reached from the spectrophotometric curves obtained.

Dinitroacetamide and dinitroacetonitrile were found to possess distinctly different ultraviolet absorption curves, i.e. dinitroacetonitrile showed weak absorption peaks at 232, 255 mμ and a strong absorbance at 345 mμ; dinitroacetamide, on the other hand, exhibited strong absorbance at 361 mμ and a broad, low maximum at 280–300 mμ. Two and one half hours after sodium dinitrocyanomethide was dissolved in concentrated hydrochloric acid, the maxima at 232, 255 and 345 disappeared completely. Instead the low, broad maxima at 280–300 mμ and the fairly sharp maximum at 361 mμ appeared. The solutions of sodium dinitrocyanomethide in concentrated hydrochloric acid were examined spectrophotometrically after 2½, 4½, 24 and 48 hr, and absorbancies at 295 and 361 mμ were compared with those from a sample of dinitroacetamide in a solution of similar pH. More than 80 per cent formation of dinitroacetamide was noted after 2½ hr. This was found to decrease to 40–50 per cent after 48 hr. Good duplication of results was obtained in successive experiments. A concentrated hydrochloric acid solution of dinitroacetamide formed *in situ* from sodium dinitrocyanomethide was further concentrated *in vacuo* at a temperature slightly above 26°C. There was no decomposition.

As mentioned previously, the identifiable contaminants accompanying dinitroacetamide were found to be dinitroacetate ester and dinitromethane. There was no difficulty in obtaining pure samples of salts of each of these, the dinitroacetates by alcoholysis of the corresponding alkyl dinitrocyanoacetates[2] and the dinitromethane salts[3] by alkaline hydrolysis of either dinitrocyanomethide or dinitroacetamide salts. Comparison of infrared spectra of dinitroacetamide, methyl dinitroacetate and dinitromethane salts indicated that detectable quantities of dinitromethane salts may have been present in most dinitroacetamide salt samples. On the other hand 3μ N–H bands and 6 μ amide carbonyl bands adequately characterized dinitroacetamide salts as parent species.

EXPERIMENTAL

Dinitroacetamide (dry hydrogen chloride). Two hundred milliliters of anhydrous ether was stirred in a closed flask which was cooled in a freezing mixture (crushed ice–isopropyl alcohol) and protected from moisture with a drying tube while dry hydrogen chloride was bubbled in until the solution was saturated at −5°. A solution of 15·3 g (0·1 mole) of dried sodium dinitrocyanomethide in a mixture of 12 ml of anhydrous methanol and 12 ml of ethyl acetate was added rapidly to the stirred, cooled ethereal hydrogen chloride solution causing the temperature to rise to 4–5°. During the next 30 min of stirring, the temperature dropped to −10°, and the reaction mixture was allowed to stand overnight immersed in the freezing mixture contained in a Dewar flask. Rapid removal of the sodium chloride formed in the reaction was best accomplished by filtration through Celite. Solvent was removed from the filtrate under reduced pressure. It was found advantageous to redissolve the concentrate in ether when it was essentially free of hydrogen chloride and to dry it with anhydrous magnesium sulfate. When solvent was then completely removed *in vacuo*, the residue crystallized and could be washed onto a filter with methylene chloride and dried. Product thus obtained has amounted to as much as 11·4 g (76·5% yield), m.p. 86–87°.

Dinitroacetamide (aqueous hydrochloric acid). Eighty-three milliliters of concentrated hydrochloric acid was cooled to −10° and stirred while 15·3 g (0·1 mole) of sodium dinitrocyanomethide was added to it in portions. The mixture was stirred for an additional hour at this temperature and was allowed to come to room temperature gradually as the freezing mixture melted. After 16 hr the temperature of

[2] Part IV: C. O. Parker, *Tetrahedron* **17**, 109 (1962).
[3] P. Duden, *Ber. Dtsch. Chem. Ges.* **26**, 3003 (1893).

the mixture was 20°. It was filtered through Celite and the filtrate was placed in a continuous liquid–liquid extractor with 800 ml of methylene chloride; extraction with boiling methylene chloride was carried out for 8 hr. Solvent was evaporated from the methylene chloride layer leaving a solid residue, which was washed onto a filter with fresh methylene chloride. The crude product weighed 2·2 g (14·7% yield) and melted at 76–77°.

Another preparation was carried out in the same manner. After filtration, the hydrochloric acid reaction mixture was diluted with an equal volume of water. This solution was extracted with 85 ml portions of isopropyl ether. The combined organic extracts were dried with anhydrous sodium sulfate and then with anhydrous magnesium sulfate. Solvent was evaporated leaving a residue which crystallized when covered with methylene chloride and seeded with dinitroacetamide crystals. There was obtained 2·1 g (14·1% yield) of crude dinitroacetamide, m.p. 48–67°.

2,2-*Dinitro*-2-*carbamylethanol*. Dinitroacetamide (24·2 g, 0·16 mole) was suspended in 20 ml of water and stirred while 13·5 ml of 37% formalin solution was slowly added dropwise. The suspended dinitroacetamide gradually dissolved but the color of the solution was never discharged. After standing overnight at room temperature, the solution was saturated with sodium chloride and extracted with ether. The ether extracts were dried with magnesium sulfate and evaporated, leaving 22 g of vacuum dried waxy yellow solid. After recrystallization from ethylene dichloride there was obtained 11·3 g (39·4% yield) of 2,2-dinitro-2-carbamylethanol, m.p. 104–107°. The infrared spectrum of this material contained bands expected for hydroxyl, amide-carbonyl (1710 cm^{-1}) and *gem*-dinitro groups (1575 cm^{-1}).

When the reaction was carried out by adding the dinitroacetamide (5·0 g, 0·033 mole) to 10 ml of formalin, the solid dissolved very rapidly with slight evolution of heat, giving a nearly colorless solution. Water was evaporated under reduced pressure and the residual, colorless oil was dissolved in ether and dried with magnesium sulfate. Evaporation of solvent and evacuation of the residue at 0·5 mm left 6·8 g (theor. yield 5·9 g). The viscous, oily product was dissolved in isopropyl ether, filtered, evaporated and evacuated again. It was not possible to induce crystallization by extensive manipulation with various solvents at low temperatures. The infrared spectrum of this material was, however, similar in most respects to that described above.

2,2-*Dinitro*-2-*carbamylethyl acetate*. A mixture of 14 g (0·02 mole) of trifluoracetic anhydride and 3·4 g (0·056 mole) of acetic acid was stirred and warmed to 50–60° under reflux for 15 min. After cooling, a solution of 10·1 g (0·056 mole) of 2,2-dinitro-2-carbamylethanol in 50 ml of ethyl ether was added with continued stirring, and the solution was heated under reflux for 1½ hr. Solvent was evaporated under reduced pressure; the residue was dissolved in methylene chloride and extracted twice with water, twice with 5% sodium bicarbonate solution and again with water. The organic portion was dried with magnesium sulfate. The dried methylene chloride solution was concentrated, cooled in a freezing mixture and diluted with petroleum ether, causing precipitation of 1·5 g (12·1% yield) of crude product, m.p. 55–58°. After three recrystallizations from a methylene chloride–petroleum ether mixture, the melting point remained constant at 60–62°.

(Found: C, 27·00; H, 2·85; N, 19·68. Calc. for $C_5H_7O_7N_3$: C, 27·15; H, 3·17; N, 19·00.)

N-(2,2-*Dinitro*-2-*carbamylethyl*) *methacrylamide*. Freshly recrystallized methacrylamide (1·7 g 0·02 mole) and 0·6 g (0·02 mole) of paraformaldehyde were ground together in a mortar. Two drops of saturated aqueous potassium carbonate solution were added to the mixture which was ground further. When the powder was warmed in a bath at 60° for a few minutes, it melted. The nearly clear melt was cooled, dissolved in 10 ml of water and filtered. To the clear filtrate was added 3 g (0·02 mole) of dinitroacetamide. The solution was warmed at 60° for 10 min, cooled, and when crystallization was complete, filtered. The dried product weighed 0·9 g (18·3% yield), m.p. 116–117°. Two recrystallizations from ethylene chloride gave a constant melting point of 120°.

(Found: C, 34·71; H, 4·32; N, 22·72. Calc. for $C_7H_{10}O_6N_4$: C, 34·15; H, 4·07; N, 22·76.)

4,4-*Dinitro*-4-*carbamylbutyric acid*. A solution of 3·0 g (0·02 mole) of dinitroacetamide in 7 ml of water was mixed with 1·4 g (0·02 mole) of glacial acrylic acid and was allowed to stand overnight at room temperature. When all volatile material was evaporated from the reaction mixture under reduced pressure, the residue crystallized. It was washed onto a filter with methylene chloride, giving 2·8 g (63·4% yield) of product, m.p. 80–95°. After two recrystallizations from ethylene dichloride, the melting point was 115–117°.

(Neut. equiv., Found: 75·0. Calc.: 73·7.)

The infrared spectrum of this material was indistinguishable from a sample of the same compound prepared in a different way.[1]

VOL. 17 1962

4,4-Dinitro-4-carbamylbutyramide. A solution of 1·4 g (0·02 mole) of freshly recrystallized acrylamide in 5 ml of methanol was mixed with a solution of 3·0 g (0·02 mole) of dinitroacetamide in 10 ml of methanol. The resulting solution was warmed at 40° for 16 hr, cooled, and a small amount of polymeric material removed by filtration. After solvent had been evaporated from the filtrate, cold water was added to the residue, causing it to crystallize. The product was filtered, washed with cold water, and when dried, weighed 2·7 g (61·3% yield); m.p. 105–106°. After two recrystallizations from ethylene dichloride, the melting point was 110–111°.

(Found: C, 27·67; H, 3·95; N, 24·42. Calc. for $C_5H_8O_6N_4$: C, 27·27; H, 3·64; N, 25·45.)

Sodium dinitroacetamide. Dinitroacetamide (5 g) was dissolved in 10 ml of methanol, the solution was stirred and methanolic sodium hydroxide solution added dropwise while cooling in an ice bath until the solution was faintly alkaline to pH paper. Crystallized salt was filtered, and dried: wt. 5·2 g, m.p. 167° dec. Recrystallization was effected by dissolving the salt suspended in boiling ethanol by addition of a little water, filtering the hot solution, cooling the filtrate and adding ether; m.p. 170° with explosion.

(Found: Na, 14·62. Calc. for $C_2H_2O_5N_2Na$: Na, 13·45.)

Potassium dinitroacetamide was prepared in analogous fashion. It was appreciably less soluble in water than the sodium salt and could be recrystallized from concentrated aqueous solution, m.p. 159° with deflagration.

Silver dinitroacetamide. A solution of 5 g of dinitroacetamide in aqueous methanol was neutralized with a solution of potassium hydroxide in methanol. The solution was warmed to dissolve any crystallized solid. A solution of 5 g of silver nitrate in 10 ml of water was added to the potassium dinitroacetamide solution causing crystallization of silver dinitroacetamide, which was filtered and dried, yield 7·6 g. Recrystallization from water gave 5·2 g, m.p. 130° with deflagration.

(Found: Ag, 44·65. Calc. for $C_2H_2O_5N_2Ag$: Ag, 42·19.)

MELTING—DECOMPOSITION POINTS OF SALTS

	Dinitroacetamide	Methyl dinitroacetate	Dinitromethane
Na	167°	212°	211–213°
K	159°	213–214°	205°
Ag	130°	168–170°	135°

Tetrahedron, 1962, Vol. 17, pp. 109 to 116. Pergamon Press, Ltd. Printed in Northern Ireland

CHEMISTRY OF DINITROACETONITRILE—IV

PREPARATION AND PROPERTIES OF ESTERS OF DINITROCYANOACETIC ACID

CHARLES O. PARKER
Rohm & Haas Co., Redstone Arsenal Research Division
Huntsville, Alabama,

VOL. 17 1962

(*Received* 23 *March* 1961)

Abstract—Nitration of oximinocyanoacetic esters with mixed acids proceeds smoothly to give good yields of esters of dinitrocyanoacetic acid.[1] A representative group of these compounds has been prepared and characterized. Reactions of dinitrocyanoacetate esters which have been studied and the products characterized include: A. Cleavage to give dinitroacetonitrile: B. Alcoholysis to give esters of dinitroacetic acid[2]: C. Reduction to give esters of nitrocyanoacetic acid.

ESTERS of dinitrocyanoacetic acid, $NCC(NO_2)_2COOR$, appear never to have been recognized previously as an easily available class of stable compounds. Nitration of oximinocyanoacetate esters, NCC(NOH)COOR, with mixed acids proceeded smoothly at or below room temperature to give good yields of dinitrocyanoacetate esters with very little evidence of decomposition or of side reactions.

The behavior of reaction mixtures appears to be compatible with the chemistry expressed by the balanced equation (1)

$$NCC(NOH)COOR + HNO_3 \xrightarrow{H_2SO_4} NCC(NO_2)_2COOR + H_2O \quad (1)$$

Under optimum conditions the products usually appeared as a separate phase in the reaction mixture and could be extracted, washed, dried and distilled or recrystallized in conventional fashion. The reaction is of general applicability; esters wherein the R-group was methyl, ethyl, isopropyl, n-butyl, cyclohexyl, β-nitratoethyl, β-bromoethyl, and *p*-nitrobenzyl were prepared, purified and identified as described below. The usual physical properties and analytical data pertaining to these compounds have been listed in Table 1.

A number of experiments were performed to determine the feasibility of preparing dinitrocyanoacetate esters directly by nitration of cyanoacetate esters, thereby avoiding isolation of the intermediate oximinocyanoacetate esters. Methyl, ethyl, isopropyl and n-butyl cyanoacetates were subjected to nitration while varying the order of mixing reagents, temperature and duration of reaction and the use of sodium nitrite and nitrosyl sulfuric acid in the reaction mixture. From methyl cyanoacetate products could be obtained containing appreciable quantities of dinitrocyanoacetate ester, identified and assayed as described below. With increasing size of the alkyl group the conversion, ease and control of reactions became progressively less satisfactory. In no case was a product obtained from which pure dinitrocyanoacetate ester could be isolated by distillation owing to the presence of unreacted starting material and various products of decomposition.

[1] C. O. Parker, U.S. Pat. 2,925,434 (1960).
[2] C. O. Parker, U.S. Pat. 2,925, 433 (1960) assignor to Rohm & Haas Co., Phila, Pa.

Dinitrocyanoacetate esters as a class of compounds exhibited three general types of degradative reactions:

(a) Susceptibility to nucleophilic attack on the carbonyl carbon atom giving rise to dinitroacetonitrile or one of its salts and a —COOR derivative of the nucleophilic agent. For example, alcohols and primary and secondary amines formed, respectively, carbonate esters and urethanes. In the presence of water, of course, the end products

TABLE 1. DINITROCYANOACETATE ESTERS, $NCC(NO_2)_2COOR$

R	b.p. (°C/mm)	n_D^{20}	Yield (%)	Found			Calculated		
				C	H	N	C	H	N
Me-	41–43/0·2	1·4370	73	25·48	1·62	21·95	25·40	1·59	22·22
Et-	55/2·5	1·4340	75	29·34	2·41	20·21	29·56	2·46	20·69
i-Pr-	48–49/0·3	1·4284	68	32·88	3·10	erratic	33·18	3·23	19·35
n-Bu-	76–80/0·06[a]	1·4359	63	36·40	2·76	18·31	36·36	3·90	18·18
Cyclo-C_6H_{11}	70–75/0·07[a]	1·4627	50[b]	40·85	3·22	14·55	42·02	4·28	16·34
$BrCH_2CH_2$-	80/0·21[a]	1·4838	86[b]	22·41	1·27	12·26	21·28	1·42	14·89
$O_2NOCH_2CH_2$-	95/0·05–0·15[a]	1·4663	51[b]	23·13	1·79	19·89	22·73	1·52	21·21
p-$O_2NC_6H_4CH_2$-	62–66[c]	—	19	[d]	—	—	—	—	—

[a] Falling film molecular distillation.
[b] Crude yield.
[c] Melting point.
[d] Identified spectrophotometrically.

included carbon dioxide and an alcohol. The experimental evidence conforms to the typical equations (2a, 2b) for these reactions:

$$NCC(NO_2)_2COOR + R'OH \rightarrow NCC(NO_2)_2H + R'OCOOR \quad (2a)$$

$$NCC(NO_2)_2COOR + 2\,R'NH_2 \rightarrow [NC\text{-}C(NO_2)_2]^-\ R'NH_2^+ + R'NHCOOR \quad (2b)$$

In a homogeneous medium this reaction proceeded spontaneously and rapidly. Serious loss of material during preparative manipulation was not experienced largely, it is believed, because dinitrocyanoacetate esters are immiscible with water. In the presence of potassium ions the very sparingly soluble potassium dinitrocyanomethide salt precipitated from any given mixture and was used both for identification and relatively accurate estimation of the quantity of dinitrocyanoacetate ester at hand.

(b) Dinitrocyanoacetate esters reacted with dry hydrogen chloride in ether alcohol solution to give some sort of intermediate which could be hydrolyzed with water giving the corresponding dinitroacetate ester in good yield. The identity of the intermediates formed in these reactions was never fully established. In several instances incomplete hydrolysis gave mixtures from which crystalline condensate appeared during distillation. The infrared spectra of these crystalline materials showed the presence of NH bands which disappeared after further hydrolysis together with the crystalline material itself. Addition of dry hydrogen chloride to an ethereal solution of a dinitrocyanoacetate ester in the absence of an alcohol failed to bring about any reaction at all. In consideration of these observations it was presumed that the crystalline material was imino-ester hydrochloride, which would be expected from normal alcoholysis of a nitrile:

$$NCC(NO_2)_2COOR + R'OH + HX \rightarrow [RO_2CC(NO_2)_2C(OR')\text{—}NH\cdot HX] \xrightarrow{H_2O}$$
$$ROOCC(NO_2)_2H + R'OCONH_2 + HX$$

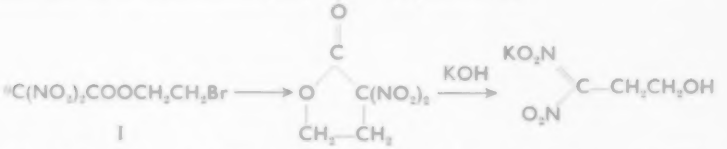
Dinitroacetate esters were isolated from several of the dinitrocyanoacetate esters

VOL. 17 1962

listed in Table 1. Physical properties and analytical data related to the dinitroacetate esters have been listed in Table 2. The stability toward distillation of crude dinitroacetate esters as isolated from hydrolysis reaction mixtures varied considerably from one ester to another. Methyl dinitroacetate and β-bromoethyldinitroacetate gave no trouble and could be distilled at once, the methyl ester conventionally and the bromoethyl ester molecularly. Conventional distillation of crude ethyl dinitroacetate preparations was unsuccessful more often than not. Thermal decomposition initiated during distillation produced quantities of diethyl furoxandicarboxylate depending upon how quickly the distilland was cooled when decomposition was noticed. However, ethyl dinitroacetate regenerated from one of its salts appeared to be completely stable toward distillation, suggesting that the presence of another species was responsible for the apparent thermal instability rather than that ethyl dinitroacetate is inherently an unstable compound.[3]

Identification of dinitroacetate esters was based upon elementary analyses of their respective salts, infrared spectra and fulfillment of expected chemical properties.

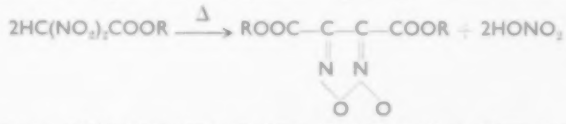
A separate problem developed from the decision to investigate the behavior of salts of β-bromoethyldinitroacetate (I). Solutions of this compound were observed to undergo spontaneous elimination of bromide ion to give a colorless crystalline product. When it was found that negatively substituted β-bromoethyl esters in general eliminated bromide ion via carbonyl oxygen displacement[4] it was considered possible that the dinitroacetate product might be α,α-dinitroketene ethylene acetal, an exotic structure. Its true identity as α,α-dinitrobutyrolactone was revealed by alkaline hydrolysis, which opened the lactone ring, cleaved the carbonyl group and yielded the potassium salt of aci-3,3-dinitropropanol-1 (equation 4).



(4)

Concerning this apparently anomalous behavior it may be observed that placing the negative charge of the anion on the carbonyl oxygen atom instead of the α-carbon atom involves moving it away from the physical center of electron density (which would appear to be at the α-carbon atom) and requires coplanarity of the two nitro groups with an adjacent carbon–carbon double bond. These conditions are evidently relatively unfavorable.

It may be of interest to mention that a few thermal decomposition reactions of aci-dinitroacetate esters were examined cursorily. The major products in each case were found to be the corresponding furoxandicarboxylic esters and nitrogen dioxide. It is believed that the reaction indicated by equation (5) proceeded rather cleanly, but insufficient attention was paid to this system to justify further comment.



(5)

[a] L. Bouveault and A. R. Wahl, *C.R. Acad. Sci. Paris*, **136**, 159 (1903), *J. Chem. Soc.* **84** I, 225 (1903); [b] A. Wahl, *Ann. Chem. Phys.* **25**, 421 (1912), *Chem. Abstr.* **1**, 1359 (1913); [c] R. S. Curtiss and J. A. Kostalek, *J. Amer. Chem. Soc.* **33**, 962 (1911).

[d] C. O. Parker, *J. Amer. Chem. Soc.* **78**, 4944 (1956).

TABLE 2. DINITROACETATE ESTERS AND SALTS, $XC(NO_2)_2COOR$

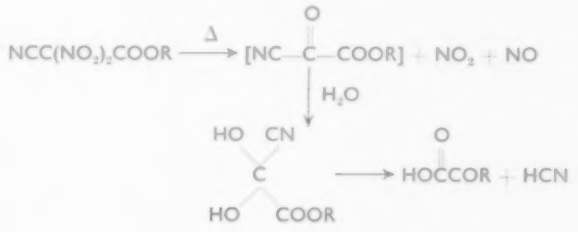
R	X	b.p.(°C/mm) or m.p. (°C)	n_D^{25}	Yield (%)	Found				Calculated			
					C	H	N	X	C	H	N	X
Me	H	38/0·02		77								
	K	213–214		52·3	18·54	1·67	13·47	19·38	17·82	1·48	13·86	19·31
	Na	212			20·19	1·86	15·17	12·42	19·35	1·61	15·05	12·36
	Ag	168–170						39·25				39·85
Et	H	54/0·05	1·4336		26·64	3·66	15·34		26·97	3·37	15·73	
	K	188–189		78	23·20	2·39	12·96	18·05	22·22	2·31	12·96	18·05
	Na	179·5–180		61	24·97	2·76	16·82	11·51	24·00	2·50	14·00	11·50
	Ag	138						37·48				37·89
n-Bu	H	[a]	1·4417	97·4								
	K	169–170		79·6	29·53	3·08	10·98	16·09	29·31	3·69	11·47	15·98
$BrCH_2CH_2$-	H	115/0·09[b]	1·4900	75								
	K	140[c]										
Cyclo-C_6H_{11}	H	[a]		80								
	K	236		69	34·28	3·60	10·03	15·68	35·42	4·05	10·33	14·39
$O_2NOCH_2CH_2$-	H	[a]		80								
	K	152·5		68	17·31	1·50	14·86	13·94	17·32	0·72	15·16	14·07

[a] Not distilled.
[b] Falling film molecular distillation.
[c] Melting point is lowered by recrystallization.

VOL. 17 1962

(c) A third type of reaction of dinitrocyanoacetate esters is one in which one of the nitro groups is reduced and the product formed is a nitrocyanoacetic ester or salt thereof. Evidence of the oxidizing character of dinitrocyanoacetate esters was provided by the rapid exothermic liberation of iodine in acetone solutions of sodium iodide. In the presence of water or alcohols, reaction according to equation (2) interfered or predominated. Interest in studying this type of reaction with a view toward finding optimum conditions for preparative use was lacking for at least three reasons. There was no particular reason for wanting a new route for the preparation of nitro cyanoacetate esters; permanganate oxidation of oximino cyanoacetate esters was a known, and serviceable method; study of the chemistry of or even isolation of nitrocyanoacetate esters was found to be somewhat troublesome on account of solubility properties. The properties of the lower alkyl nitrocyanoacetate esters curiously seemed to resemble the properties of dinitroacetonitrile except that no sparingly soluble salts were found. Consequently, the reduction of dinitrocyanoacetate esters was examined only very briefly. The potassium salt of ethyl nitrocyanoacetate, isolated from treatment of ethyl dinitrocyanoacetate with hydrobromic acid in ethanol, was identified by correspondence of melting point, infrared spectra and lack of mixed melting point depression with an authentic sample.

In one experiment thermal decomposition of isopropyl dinitrocyanoacetate was performed. Only one major gaseous product was formed, namely nitrogen dioxide with accompanying minor quantities of nitric oxide, carbon dioxide and hydrogen cyanide. There was a liquid residue which crystallized when cooled and could be sublimed. It dissolved in water to give an acid solution containing hydrogen cyanide. From consideration of its infrared spectrum, neutral equivalent and cyanide ion determinations it appeared that the product of the reaction might be an α,α-dihydroxy cyanoacetate, formed by combination of a probable keto-precursor with adventitious moisture. The suggested relationships are shown in equation (6).



(6)

EXPERIMENTAL

The series of dinitrocyanoacetate esters listed in Table 1 were prepared from corresponding oximinocyanoacetate esters which in turn were obtained by nitrosation of cyanoacetate esters. Since several of these have not been reported previously the physical properties and analytical data related to the oximinocyanoacetate and cyanoacetate ester intermediates have been listed in Tables 3 and 4, respectively.

Nitrosation of cyanoacetate esters proceeded readily at pH 4, 5. In all cases it was found desirable to avoid the use of acetic acid, because of the difficulty in removing it from the oximinoester product.[5]

[5] K. N. F. Shaw and C. Nolan, *J. Org. Chem.* **22**, 1668 (1957) described addition compounds of oximinomalonates with sodium acetate. Considering the tenacity with which acetic acid is retained by oximinomalonates and oximinocyanoacetates it seems likely that coordination of some sort exists with acetic acid also.

TABLE 3. OXIMINOCYANOACETATE ESTERS, NCC(NOH)COOR

R	m.p. (°C)	Yield (%)	Found			Calculated		
			C	H	N	C	H	N
n-Bu	89–91	76	49·53	5·59	16·54	49·41	5·88	16·47
Cyclo-C_6H_{11}-	104–105·5	53	56·40	6·78	13·54	55·10	6·12	14·29
$BrCH_2CH_2$-	113·5–115·5	80	27·62	1·93	12·15	27·15	2·26	12·67
$O_2NOCH_2CH_2$-	98–98·5	27	29·20	2·50	19·60	29·56	2·46	20·69
p-$O_2NC_6H_4CH_2$-	158–160	26	[a]					

R = Me, 68% yield, m.p. 122–124; Et, 95%, 129–131°; i-Pr, 51%, 105–107°

[a] Identified spectrophotometrically.

TABLE 4. CYANOACETATE ESTERS, $NCCH_2COOR$

R	b.p. (°C/mm)	n_D^{20}	Yield (%)	Found			Calculated		
				C	H	N	C	H	N
n-Bu	73–74/0·28	1·4260	93	59·87	7·45	12·01	59·57	7·80	9·93
Cyclo-C_6H_{11}	91–92/0·24	1·4621	94	64·70	7·29	8·14	64·67	7·78	8·38
$O_2NOCH_2CH_2$-	105–106/0·035	1·4573	53	34·41	2·94	16·01	34·48	3·45	16·09
p-$O_2NC_6H_4CH_2$-	68–69[a]	—	39	—	—	—	—	—	[b]

R = Me, Et commercial samples; R = i-Pr, n_D^{20} 1·4168

R = $BrCH_2CH_2$- (Ref. 3, general method of preparation)

[a] Melting point.

[b] Identified spectrophotometrically.

Ethyloximinocyanoacetate. Three hundred and thirty-nine grams of ethyl cyanoacetate (2·00 moles) was suspended in a vigorously stirred solution of 194 g sodium nitrite (4·16 moles) in 2400 ml of water. The slow dropwise addition of 210 g of 85% phosphoric acid (1·83 moles) was begun. The rate of addition was such as to maintain a pH of 4.5 while the temperature of the reaction mixture was kept at 35–40°C by application of an external cooling bath. The addition of acid required about 30 min. After the solution was stirred for an additional hour at 30°, 252 ml of concentrated hydrochloric acid was added while the temperature of the reaction mixture was raised to 50° to prevent the premature precipitation of ethyl oximinocyanoacetate. The acidified solution was allowed to cool slowly to −10°. The precipitated ethyl oximinocyanoacetate was collected on a filter and then dried for 4 hr in a vacuum oven at about 50°C. An additional 35–45 g of ethyl oximinocyanoacetate was recovered by extraction of the filtrate with one 500 ml portion of ether. The total product amounted to 425 g (100% yield).

Ethyl dinitrocyanoacetate. Ninety-six grams (0·94 mole) of concentrated sulfuric acid was added dropwise to 30·5 g (0·47 mole) of anhydrous nitric acid while the mixture was stirred at 5–10° in a flask protected from moisture with a drying tube. To this solution, 28·4 g (0·2 mole) of ethyl oximinocyanoacetate was added portionwise at the same temperature. The reaction mixture became turbid soon after addition of the oximinoester was begun and heat evolution ceased soon after addition was completed. The mixture was stirred for 1½ hr while the temperature was controlled at 15–20°. The lower layer of acids was drained and quenched; the upper layer (34 g) was extracted into methylene chloride solution, washed three times with cold water and dried with anhydrous magnesium sulfate. Solvent was evaporated and the residue distilled giving 30·4 g (75% yield) of product, b.p. 36–37°/0·08 mm., n_D^{20} 1·4332. A portion of this material was redistilled and a middle cut of distillate taken for analysis (see Table 1).

Dinitrocyanoacetate esters were observed to have similar characteristic infrared absorption spectra containing bands attributable to cyano, carbonyl and dinitrocyanomethyl groups. In the spectra of

the methyl and ethyl esters these bands were centered at 2240 cm^{-1}, 1784, 1790 cm^{-1} and 1610 cm^{-1} respectively.

Nitration of methyl cyanoacetate. To a colorless mixture of 25·2 g (0·4 mole) of anhydrous nitric acid and 81·6 g (0·8 mole) of sulfuric acid, 28·4 g (0·2 mole) of methyl cyanoacetate was slowly added dropwise. The mixed acids were stirred initially at 20° and the temperature was controlled at 30° during the addition. Very slow gassing was observed. After stirring for 30 min longer, the temperature was lowered to 5° and the reaction mixture was left in an ice bath in a Dewar flask overnight. The separated upper layer in the reaction mixture was extracted into methylene chloride and this solution was extracted with three portions of water and dried with anhydrous magnesium sulfate. Evaporation of solvent left 13·89 g (36·5% yield) of crude product. The infrared spectrum of this material showed it to be identical with methyl dinitrocyanoacetate prepared from the oximinoester.

VOL. 17 1962

Reaction of ethyl dinitrocyanoacetate with aniline. A solution of 2·0 g (0·01 mole) of ethyl dinitrocyanoacetate in ether was stirred and kept at 15° with an ice bath while 1·6 g (0·02 mole) of aniline was added to it dropwise. After an additional 10–15 min at 15–20°, the solution was filtered. It was found necessary to wash the light colored crystalline product very thoroughly with ethyl ether before it could be dried and kept exposed to air without darkening. The yield if anilinium dinitrocyanomethide was 2·0 g (89%), m.p. 152–153°.

The filtrate from the reaction mixture was washed with water, with sodium bicarbonate solution, with dilute hydrochloric acid, and with water again. It was dried with anhydrous sodium sulfate and evaporated. The residue crystallized when it was chilled and scratched. It was treated with two successive portions of charcoal in ethanol solution before a white product could be obtained by addition of water. The yield of phenyl urethane was 0·6 g (36%), m.p. 49–50° (lit., m.p. 53°).

Reaction of ethyl dinitrocyanoacetate with ethanol. To 25 ml of ethanol freshly distilled from magnesium ethoxide 16·9 g (0·083 mole) of ethyl dinitrocyanoacetate was added dropwise. The addition caused a noticeable exotherm which was controlled at 30° by external cooling. After standing overnight at room temperature, ethanol was carefully distilled from the mixture at 40°. Addition of three volumes of water to the distillate caused separation of a non-aqueous layer. The residue from the distillation was added to an excess of aqueous bicarbonate solution. This mixture was extracted with ethyl ether. The ether extracts and the non-aqueous portion of the distillate were combined, washed with bicarbonate solution and dried. Evaporation of the ether left 7·7 g of liquid residue, which was distilled at atmospheric pressure giving 5·8 g (59% yield) of diethyl carbonate, b.p. 122–124°. Addition of excess potassium chloride solution to the bicarbonate solution of the reaction mixture residue gave 9·1 g (65% yield) of potassium dinitrocyanomethide, m.p. 266–268°.

Ethyl dinitroacetate. Dry hydrogen chloride was passed into a solution of 40·6 g (0·2 mole) of ethyl dinitrocyanoacetate in 500 ml of absolute ethyl ether while the solution was cooled in an ice bath. When the solution temperature dropped from 10° to 2°, addition of 75 ml of ethanol, distilled from magnesium into the dropping funnel was begun. Addition of hydrogen chloride was continued to saturation. After the solution had stood overnight at room temperature, excess hydrogen chloride and ether were distilled until the pot temperature reached 50°. During this time a small quantity of white solid precipitated from solution. Remaining solvent was evaporated under reduced pressure. The residue was dissolved in two volumes of methylene chloride, extracted three times with cold water and dried with magnesium sulfate. Incomplete hydrolysis was effected by this washing procedure. Solvent was removed and the residue was distilled. After 2–3 ml of forerun (56–62°/0·15 mm) the distillate crystallized in the condenser. A sample (a) of the crystallized distillate was obtained before the rest of the material was distilled, b.p. 58°/0·1 mm to 75°/0·3 mm without crystallizing. An infrared spectrum of (a) showed it to be a mixture containing an N—H doublet band at 3 μ double carbonyl bands at 1760 and 1708 cm^{-1}, and a nitro band at 1588 cm^{-1}. (In ethyl dinitrocyanoacetate the carbonyl and nitro bands occur at 1780 and 1600 cm^{-1}, respectively.) The main portion of distillate was then shaken with one volume of ice-cold concentrated hydrochloric acid. The organic layer was separated, dissolved in methylene chloride, extracted once with cold water, dried and redistilled, yielding 15·1 g of colorless distillate, b.p. 50–54°/0·05 mm. The infrared spectrum of this material showed strong carbonyl and nitro bands at 1767 and 1584 cm^{-1}, respectively. The 3 μ N—H doublet and carbonyl band at 1708 cm^{-1} were no longer present. Titration with base gave an equivalent weight of 177. (Theoretical neutral equivalent, 178.)

A 10 g sample of distilled product was treated with alcoholic potassium hydroxide solution giving a bright yellow potassium salt. The salt was recrystallized once from ethanol, m.p. 187° dec. Five grams of this salt were suspended in 10 ml of water and were treated with sulfuric acid dropwise until

the solution was acid to Congo red. The acidified solution was extracted with ether, the extracts were dried and the residue after evaporation of solvent was distilled, giving 3·5 g of colorless distillate, b.p. 35–37°/0·025 mm. The equivalent weight (180) and infrared spectrum of the recovered nitro ester showed it to be identical with the product before conversion to its salt.

β-Bromoethyl dinitrocyanoacetate. The crude product (residue from dried methylene chloride solution; see ethyl ester) obtained from the nitration of 118 g (0·53 mole) of β-bromoethyl oximinocyanoacetate with 83·8 g (1·33 moles) of absolute nitric acid and 272·3 g (2·67 moles) of concentrated sulfuric acid, weighed 128·9 g (0·457 mole, 86% yield). This material was dripped slowly through a falling film still, collecting the distillate and returning the undistilled portion for successive passes. At 60°/0·2 mm only 2·0 g of distillate was collected. On the next pass at 80°/0·2 mm, 54·8 g distillate (n_D^{20} 1·4826) was obtained. The residue passed through at 82°/0·13 mm gave 28·6 g of distillate, n_D^{20} 1·4830. The residue weighed 40·3 g, n_D^{20} 1·4850. Comparison of infrared spectra showed no significant different between the fractions of distillate and the undistilled residue. The analytical data (Table 1) was obtained from another preparation which was subjected to a wider temperature range during distillation.

β-Bromoethyl dinitroacetate. A solution of 38 ml of commercial absolute methanol in 150 ml of commercial anhydrous ether was saturated with hydrogen chloride gas taken directly from a cylinder. The solution temperature was reduced to 0–5° by external cooling when HCl vapor began to emerge through the exit drying tube. Dropwise addition of 53·2 g (0·189 mole) of distilled β-bromothyl dinitrocyanoacetate to the stirred solution at 0–5° was then carried out while continuing addition of hydrogen chloride. The reaction mixture was allowed to stand idle at 0° overnight. Stirring was resumed while the mixture was cooled in an ice bath and 38 ml of water was added slowly dropwise. The reaction mixture was stirred while the temperature was allowed to rise to 25° during the course of an hour. The apparatus was dismantled and the reaction mixture was poured into 400 g of ice and water. The cold mixture was extracted successively with three 100 ml portions of methylene chloride. The combined extracts were skaken with two 100 ml portions of cold water and dried with anhydrous magnesium sulfate. Evaporation of solvent left 44·6 g of crude residue. Infrared examination of the crude product showed hydrolysis to be nearly complete by the negligible proportions of the N—H doublet. Distillation through the falling film still at 115°/0·09 mm gave 36·5 g (75% yield) of distillate. In the infrared spectrum of β-bromoethyl dinitroacetate the carbonyl and nitro-group absorption bands were centered at 1770 and 1587 cm^{-1} respectively.

Potassium salt of β-bromoethyl dinitroacetate. Dropwise addition of a solution of 0·6 g (0·01 mole) of potassium hydroxide in 10 ml of ethanol to a cold solution of 2·6 g (0·01 mole) of β-bromoethyl dinitroacetate in 25 ml of ethanol caused precipitation of white salt. The cold solution was filtered and the solid on the filter washed with cold ethanol and then with ether. Dried product wieghed 2·3 g m.p. 145–150° dec. Dissolution of this salt in any solvent, e.g. ethanol, acetonitrite, acetone, ethyl acetate, resulted in recovery of product having a lower melting point. Material precipitated from ethyl acetate solution with ether, m.p. 136° dec., gave an analysis consistent with the composition of a mixture of 91·3% $C_4H_4O_6N_2BrK$ with 8·7% KBr.

α,α-Dinitro-γ-butyrolactone. A solution of the potassium salt of β-bromoethyl dinitroacetate in acetone was heated under reflux for 4 hr, cooled and filtered to remove precipitated potassium bromide. The filtrate was allowed to stand idle overnight. Additional potassium bromide was removed by filtration; solvent was evaporated from the filtrate and the residue was extracted into chloroform solution, filtered and the filtrate concentrated until crystallization occurred. The product was recrystallized again from chloroform, giving pure, white solid, m.p. 64·5–65·5°.

(Found: C, 27·56; H, 2·28; N, 15·39. Calc. for $C_4H_4O_6N_2$: C, 27·27; H, 2·27; N, 15·91.)

Direct titration with standard alkali, which produced a yellow solution, gave a neutral equivalent of 140 (theor. 176) with a fading end point. Back titration of excess alkali gave a neutral equivalent value of 90; this is consistent with cleavage of the molecule to form the salt of γ,γ-dinitropropanol-1 together with bicarbonate.

α,α-Dinitro-γ-butyrolactone dissolved in aqueous potassium hydroxide solution with evolution of heat. The solution was evaporated to near dryness causing crystallization of a yellow solid. The residue was washed onto a filter with ethanol and was recrystallized from boiling ethanol by addition of a little water, m.p. 147 dec. The infrared spectrum of this product was identical with that of a sample of the potassium salt of γ,γ-dinitropropanol-1, obtained by treating γ-nitro propylnitrate with potassium hydroxide.

Tetrahedron, 1962, Vol.17, pp. 117 to 122. Pergamon Press, Ltd. Printed in Northern Ireland

VOL. 17 1962

AMINE BORANES—X

ALKYLIDENEAMINO t-BUTYLBORANES. THE HYDROBORATION OF NITRILES WITH TRIMETHYLAMINE t-BUTYLBORANE

M. FREDERICK HAWTHORNE*
The Rohm & Haas Company, Redstone Arsenal Research Division, Huntsville, Alabama

(*Received* 17 *May* 1961)

Abstract—The hydroboration of aliphatic and aryl nitriles with trimethylamine t-butyl borane results in the formation of 1:1 adducts, RCH—NBHt—Bu. The principal products have been shown to be nitrogen-bridged cyclic dimers. Thermal soaking of the dimeric products results in the quantitative formation of less soluble and higher-melting materials which are either stereoisomers or stoichiomers. The reactions of dimeric benzylideneamino t-butylborane include acid hydrolysis to yield benzaldehyde.

THE reaction of acetonitrile with diborane has been reported to yield an adduct, $CH_3CN{\cdot}BH_3$ which is in part converted to N,N′,N″-triethylborazine upon pyrolysis.[1] More recent studies of the reactions of acetonitrile, n-propionitrile, benzonitrile and acrylonitrile with diborane have reaffirmed the existence of such 1:1 borane-nitrile adducts which were not well characterized.[2] Brown and Subba Rao[3] have shown that diborane may function as a reagent for the reduction of nitriles to the corresponding primary amine. In view of the facile hydroboration of 1-alkenes and 1-alkynes with trimethylamine t-butylborane,[4] it was of compelling interest to examine the reactions of this sterically encumbered borane derivative with representative nitriles.

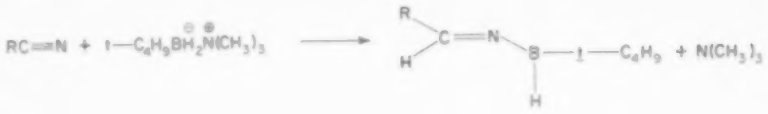
RESULTS AND DISCUSSION

Aliphatic nitriles. Acetonitrile, propionitrile, n-butyronitrile and i-butyronitrile were each treated with an equimolar quantity of trimethylamine t-butylborane in diglyme solution at 100°. Trimethylamine was smoothly evolved. Fractional distillation of the reaction mixtures at reduced pressure afforded low yields of high-boiling products. In every case except that of n-butyronitrile, these products crystallized on standing at room temperature. Further purification was obtained by recrystallization from ethanol. Analyses indicated these materials to be 1:1 adducts of t-butylborane and the starting nitrile. The melting point ranges observed with these materials suggested that they were not homogenous although a good crystalline habit was always observed after the first recrystallization. The i-butyronitrile product melted at 58–60°, resolidified and melted again at 110°. The molecular weight of each product was determined by the cryoscopic method in benzene solution and corresponded to that of dimer. The infrared spectrum of each product contained a B–H stretching band at 2390 cm^{-1} and a C=N stretching band at 1660 cm^{-1}. The B^{11} NMR spectra of the liquid n-butyronitrile and the crystalline acetonitrile products displayed doublets

* Visiting lecturer, Harvard University, Fall 1960

[1] A. B. Burg, *Rec. Chem. Progr.* (*Kresge-Hooker Sci. Libr.*) **15**, 159 (1954).
[2] H. J. Emeleus and K. Wade, *J. Chem. Soc.* 2614 (1960).
[3] H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.* **82**, 681 (1960).
[4] M. F. Hawthorne, *J. Amer. Chem. Soc.* In press.

with $\delta = +9{\cdot}9 \times 10^{-6}$ and $+19{\cdot}2 \times 10^{-6}$ relative to trimethyl borate. This evidence and that cited above leaves no doubt that these products are dimers of alkylideneamino t-butylboranes formed by bridging boron atoms through the alkylideneamino groups.[5] Thus the overall reactions may be written



The stereochemical consequences of this formulation will be discussed below. Characterization data for these materials are presented in Table 1.

Aryl nitriles. In accord with the results described above, benzonitrile and its *p*-methoxy-, *p*-chloro-, *p*-fluoro, *p*-methyl and *m*-methyl derivatives yielded crystalline, high melting products when treated with trimethylamine t-butylborane in diglyme solution at 100°. In each of these cases, except that of the *m*-methyl derivative, the crude crystalline products were separated into two pure crystalline fractions. The fraction formed in highest yield in each system was always found to be the lower melting and to display usefully high solubility in common organic solvents. Analyses of each pair of reaction products proved their compositions to be that of 1:1 adducts of the starting nitrile and t-butylborane. In general, the more soluble member of each pair of products melted near 140° while the less soluble member melted near 190°. It was observed that the lower-melting materials resolidified when heated above their melting points and again melted near the melting point of the higher-melting fraction. The conversion of the lower-melting member to the higher-melting member of the benzonitrile product pair was quantitatively accomplished by fusion. The infrared spectrum of the fused product was identical to that of the higher-melting member.

Examination of the infrared spectrum of each of the compounds described above in a Nujol mull revealed the following facts. In every case a C=N stretching band was observed at 1640 cm^{-1}. Significant differences were observed in the fingerprint region from compound to compound but these differences could not be correlated with the melting point and solubility properties. Every member of the lower-melting series of hydroboration derivatives except those derived from *p*-methoxy- and *m*-methylbenzonitriles, displayed a B—H stretching doublet at 2350 and 2400 cm^{-1}. The two exceptions gave sharp B—H stretching at 2350 cm^{-1} as did every member of the higher-melting series. The apparent B—N stretching doublet of the lower-melting series was observed as a sharp singlet at 2350 cm^{-1} in methylene chloride solution. Thus, this anomaly is undoubtedly a result of interactions in the crystalline state.

[5] Methylamino t-butylborane dimer displays a doublet in its B^{11} NMR spectrum with $\delta = +9{\cdot}7$ and $+18{\cdot}0$.

Molecular weight determinations were made with each member of the more soluble series of derivatives. The cryoscopic method was employed in benzene solvent. In each case the lower-melting and most soluble products proved to be dimers. That these dimers are nitrogen-bridged was indicated from the position of the B^{11} NMR resonances obtained with the benzonitrile product. A doublet was observed with $\delta = +10$ and $+20$ in acetonitrile solution relative to trimethyl borate.

Table 1 reports the characterization data obtained for the derivatives of any nitriles.

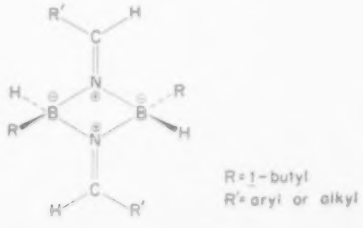
If, as the facts presented above indicate, the new materials described in this study are nitrogen-bridged stoichiomers of aldylideneamino t-butylboranes, one would expect the substituted benzylidene derivatives to absorb strongly in the ultraviolet. This was observed. The higher-melting benzylidene derivative had λ_{max} 274 mμ, ε 9000 and the lower melting member λ_{max} 273 mμ, ε 11,400. The corresponding *p*-methoxy compounds had λ_{max} 302 mμ, ε 18,500 and λ_{max} 302 mμ, ε 18,000, respectively. Extinction coefficients were calculated on the basis of monomer molecules. Short wave-length absorption was not well defined. In contrast, the products derived from aliphatic nitriles exhibited end absorption only.

Additional evidence for the assumed structure of the nitrile-t-butylborane adducts was obtained from the acid hydrolysis of the benzonitrile product in aqueous ethanol. Benzaldehyde was isolated in 48 per cent yield from the hydrolysis of the lower-melting member of the product pair. Hydrogen and t-butylboronic acid were also observed as reaction products. The hydrolysis reaction is described by the equation

$$(\text{t-}C_4H_9BHN{=}CH\phi)_2 + 2H_3O^{\oplus} + 4H_2O \rightarrow$$
$$2\phi CHO + 2H_2 + 2NH_4^{\oplus} + 2\text{t-}C_4H_9B(OH)_2$$

Stereochemistry and stoichiomers. As shown above, the hydroboration products derived from aliphatic nitriles and the lower-melting, more soluble products derived from aryl nitriles are dimers. The position of the B^{11} NMR resonances of these compounds prove that they are nitrogen-bridged. Such cyclic structures present a number of possible stereoisomers. Thus, the bulky t-butyl groups could be *cis-* or *trans-* with respect to each other and the alkylidene or benzylidene amino groups could assume a *syn* or an *anti-* arrangement. Thus, *cis-syn*, *cis-anti*, *trans-syn* and *trans-anti* configurations are possible. Of these possibilities the *trans-anti* isomer (I) would be predicted to be the more stable.

The question arises as to the nature of the higher-melting products obtained directly



I

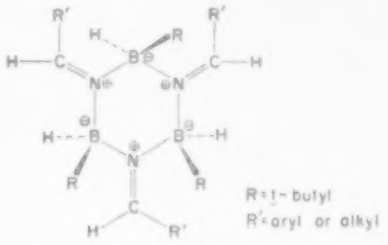
TABLE I. ALKYLIDENEAMINO AND SUBSTITUTED BENZYLIDENEAMINO t-BUTYLBORANES

R in RCH=NBHt-Bu	Yield (%)	m.p. (b.p./mm) °C	Found (%)				Calc. (%)			
			C	H	N	B	C	H	N	B
Methyl	22	75–78(72–78/0·8)	64·88	12·72	12·37	9·83	64·92	12·71	12·62	9·75
Ethyl	20	79–83(84–93/0·8)	67·28	12·67	11·07	8·77	67·24	12·90	11·20	8·65
n-Propyl	40	(86–88/0·1)	68·84	12·82	10·18	7·69	69·10	13·05	10·07	7·78
i-Propyl	41	57–60*(84–94/0·4)	69·15	13·16	9·95	7·79	69·10	13·05	10·07	7·78
Phenyl	63	141–143	76·16	9·32	8·21	6·52	76·33	9·31	8·10	6·26
	6·5	191–193	76·56	9·37	7·99	6·29	76·33	9·31	8·10	6·26
p-Methoxyphenyl	89	145–146	70·81	8·87	6·90	5·52	70·96	8·93	6·90	5·33
	9·5	185–187	70·89	9·02	7·21	5·58	70·96	8·93	6·90	5·33
p-Chlorophenyl	74	138–140	63·53	7·47	6·65	5·40	63·66	7·28	6·75	5·21
	8·2	190–191	63·67	7·21	6·87	5·40	63·66	7·28	6·75	5·21
p-Fluorophenyl	93	137–139	69·18	8·20	7·44	5·72	69·15	7·91	7·33	5·66
	0·5	180–182	69·32	8·18	7·55	5·83	69·15	7·91	7·33	5·66
p-Methylphenyl	89	146–148	77·28	9·60	7·28	5·56	77·03	9·70	7·49	5·78
	6	187–188	76·95	9·75	7·46	5·75	77·03	9·70	7·49	5·78
m-Methylphenyl	90	124–126	76·88	9·91	7·49	5·48	77·03	9·70	7·49	5·78

* Second melting point observed at 110° on continued heating.

during the hydroboration reaction or formed by thermal treatment of the lower-melting products.

Since thermal rupture of a B-N bond in the 4-membered cyclic dimers provides a possible mechanism for both *cis-trans* and *syn-anti* interconversions it is reasonable to assume that every isolated dimer species has the preferred stereochemistry shown in I. The markedly great change in properties which occurs upon heating these dimers suggests that the higher-melting products are not mere stereoisomers of the lower-melting dimers but are actually higher stoichiomers of optimum stereochemistry such as 6-membered, nitrogen-bridged cyclic trimers (II). If the trimer ring is in the chair



II

configuration, then a *cis*-equatorial arrangement of t-butyl groups would most likely prevail.

EXPERIMENTAL

Materials. Nitriles were commercially available materials of high purity. Trimethylamine t-butylborane was prepared as previously described[4] and used without further purification. The diglyme employed was purified by distillation from lithium aluminium hydride at reduced pressure.

Preparation of alkylideneamino t-butylboranes. To a solution of 0·10 mole of the aliphatic nitrile dissolved in 25 ml of diglyme at 100° was added 13·0 g (0·10 mole) of crude trimethylamine t-butylborane. The addition was carried out in a dropwise fashion in a nitrogen atmosphere and with magnetic stirring. The addition required 1 hr. The reaction mixture was then heated for one additional hour and cooled to room temperature. The reaction product mixture was added to 200 ml of water and the oily product separated by extraction with diethyl ether. The ether extract was washed three times with 50 ml portions of water, separated, dried over magnesium sulfate and evaporated at reduced pressure. The residual oil was transferred to a small still pot and fractionated with a spinning band distillation column at reduced pressure. Table 1 reports yields, boiling points and melting points of crystallized distillates. Analytical samples were prepared by recrystallization from ethanol–water.

Preparation of substituted benzylideneamino t-butylboranes. One tenth mole of the proper substituted benzonitrile was dissolved in 25 ml of diglyme and treated with 13·0 g (0·10 mole) of trimethylamine t-butylborane as described above. Following the heating period the product mixture was treated with 200 ml of diethyl ether and filtered. The filtrate was washed well with water, dried over magnesium sulfate and the solvent removed at reduced pressure. The ether insoluble product was recrystallized from acetonitrile or benzene. The ether soluble product was recrystallized from acetonitrile or ethanol–water. Table 1 provides the yields, melting points and analytical data obtained for these products.

Conversion of the lower-melting benzylideneamino t-butylborane product to the higher-melting product. One gram of the ether soluble product derived from benzonitrile (m.p. 141–143°) was placed in a small flask equipped with a nitrogen inlet and outlet. The flask was heated by an oil bath and the temperature slowly raised from 140° to 162°. During this interval the product melted and crystallized. The flask was then heated to 169°, cooled and the crystalline product washed with diethyl ether. The product melted at 185–189° and was identical to the authentic higher-melting product in the infrared.

Preparation of benzaldehyde from benzylideneamino t-butylborane. To a cooled solution of 20 g

of concentrated sulfuric acid in 60 ml of 25% aqueous ethanol was added 17·3 g (0·10 mole) of the lower-melting benzylideneamino t-butylborane. The mixture was gently refluxed under nitrogen for 12 hr, cooled and added to 400 ml of water. The products were separated by three extractions with diethyl ether. The combined ethereal extracts were evaporated to dryness under reduced pressure. An infra-red spectrum of the crude product indicated it to be a mixture of t-butylboronic acid and benzaldehyde.

The crude product was dissolved in 75 ml of ether and the ethereal solution extracted three times with 100 ml portions of 10% sodium bisulfite. The aqueous extract was then treated with 100 g of potassium bicarbonate and the liberated benzaldehyde extracted with three 50 ml portions of diethyl ether. The combined ether extracts were dried over magnesium sulfate and the ether removed by evaporation at reduced pressure at $-10°$. The product was shown to be pure benzaldehyde by infra-red identification and weighed 5·1 g or 48% of theory.

Molecular weight determinations. Molecular weight determinations were carried out in duplicate using a conventional cryoscopic apparatus and dry benzene as solvent. Results were reproducible and agreed with theory to within ±2%.

Nuclear magnetic resonance measurements. A Varian high resolution nuclear magnetic resonance spectrometer was employed with a 12·8 mc B^{11} probe. Benzene was routinely employed as solvent and a capillary tube which contained trimethylborate provided the reference resonance.

Acknowledgement—The work was carried out under U.S. Army Ordnance Contract DA-01-021-ORD-11878.

TETRAHEDRON

Contributed Symposia on Recent Developments in Organic Chemistry

VOL.
17
1962

NUMBER 3

AN EPISTOLOGUE ON CARBON BONDS

Convened and Edited by

M. J. S. DEWAR

University of Chicago, Chicago 37, Illinois, U.S.A.

VOL.
17
1962

Contributors to the Epistologue on Carbon Bonds

L. S. BARTELL, Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.

O. BASTIANSEN, Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway.

C. A. COULSON, Mathematical Institute, Oxford, England.

D. W. J. CRUICKSHANK, School of Chemistry, The University, Leeds, England.

R. DAUDEL, Centre de Mecanique Ondulatoire Appliquee, 155 Rue de Sévres, Paris, France.

MICHAEL J. S. DEWAR, George Herbert Jones Laboratory, University of Chicago, Illinois, U.S.A.

W. T. DIXON, Mathematical Institute, Oxford, England.

INGA FISCHER-HJALMARS, Division of Mathematical Physics, The Royal Institute of Technology, Stockholm 70, Sweden.

M. I. KABACHNIK, The U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

DAVID R. LIDE, JR., National Bureau of Standards, Washington 25, D.C., U.S.A.

J. D. MARAIS, Merensky Institute for Physics, University of Stellenbosch, Stellenbosch, South Africa.

T. A. MASTRYUKOVA, The U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

T. A. MELENT'YEVA, The U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

R. B. MURPHY, Department of Chemistry, University of Washington, Washington, U.S.A.

LUIGI OLEARI, Instituto di Chimica Generale, University of Padua, Padua, Italy.

LINUS PAULING, California Institute of Technology, Pasadena, California, U.S.A.

J. ROBINS, Department of Chemistry, University of Washington, Washington, U.S.A.

W. M. SCHUBERT, Department of Chemistry, University of Washington, Washington, U.S.A.

N. SHEPPARD, University Chemical Laboratory, Lensfield Road, Cambridge, England.

B. P. STOICHEFF, Division of Pure Physics, National Research Council, Ottawa, Canada.

M. TRÆTTEBERG, Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway.

E. BRIGHT WILSON, JR., Mallinckrodt Chemical Laboratory, Harvard University, Cambridge 38 Massachusetts, U.S.A.

Tetrahedron, 1962, Vol. 17, p. 123. Pergamon Press Ltd. Printed in Northern Ireland

VOL.
17
1962

INTRODUCTION

EPISTOLOGUE ON THE EFFECT OF ENVIRONMENT ON THE PROPERTIES OF CARBON BONDS

MICHAEL J. S. DEWAR
George Herbert Jones Laboratory, University of Chicago

WITH the steady growth of science it has become increasingly difficult for scientists to keep in touch with one another and to discuss their problems. This has led to what might be called the Conference Explosion, a proliferation of conferences, symposia, discussions, and meetings of all kinds. This has proved an inadequate solution for three reasons. First, it is difficult to collect all the leading workers in any field together at any one place and time; secondly, such meetings are very time-consuming; and thirdly, it is almost impossible to have a satisfactory discussion at a meeting where the participants have not seen the papers in advance and where there is often a large paying audience anxious to get its money's worth by pouncing on any ill-considered comment.

The last difficulty can be avoided by circulating preprints of the papers to the participants before the actual meeting is held; this is done with great effect by the Faraday Society, to take one example. The difficulty still remains, however, of bringing together all the people who should be there to discuss some specific branch of science.

Some years ago the Editorial Board of *Tetrahedron* introduced a series of "Paper Symposia", each consisting of a set of invited papers on some specific topic which were published together in one issue. When I was asked to organize such a symposium it occurred to me that it would be made much more valuable if the contributed papers were circulated to the participants so that points raised could be discussed and the discussion published. This we have now done; and we present here the first *Epistologue*, on the Effect of Environment on the Properties of Carbon Bonds. Since this is a new kind of publication, destined to reduce Conferences to their proper (and occasional) place, we felt it ought to have a new name. The term Epistologue (ἐπιστολή + λόγος) seemed appropriate, implying a discussion by correspondence. The idea could of course be extended. The papers could for example be circulated to others working in the same field who did not wish to contribute papers but had comments to make. Here there was not time to develop this possibility to any extent but Professor Mulliken has taken part on this basis.

The subject of the Epistologue is one of great topical interest and the papers and authors need no introduction. As the organizer I felt I should keep quiet.

Tetrahedron, 1962, Vol. 17, pp. 125 to 134. Pergamon Press, Ltd. Printed in Northern Ireland

A SURVEY OF CARBON–CARBON BOND LENGTHS

DAVID R. LIDE, JR.
National Bureau of Standards, Washington 25, D.C.

(*Received* 3 *January* 1961)

Abstract—The operational definitions of bond length are discussed. The importance of using bond lengths determined by the same experimental method when looking for small variations is emphasized. A survey is given of recent measurements of C=C and C≡C bonds and of the various types of CC single bonds. The single bond lengths may be fitted by a set of orbital radii which depend on the hybridization state of the carbon atom. Bonds between carbon and nitrogen, oxygen, fluorine, chlorine, and silicon are also discussed. While variations in CC bond lengths can be satisfactorily explained on the basis of hybridization being the major factor, it appears necessary to introduce electron delocalization effects when atoms with lone pairs are involved. It is shown that bond angles do not provide a reliable measure of the carbon hybridization.

VOL. 17 1962

INTRODUCTION

IT is probably fair to say that bond lengths have been more widely used than any other molecular property for providing an insight into the nature of the chemical bond. Even with very crude measurements of bond length, it has been possible to detect some of the gross effects of molecular environment upon the bond between two given atoms. As theories of molecular structure have been refined, there has been a tendency to attach significance to smaller and smaller variations in measured bond lengths. While experimental techniques have improved concurrently, the correspondence has not always been one-to-one. In the case of carbon–carbon bond lengths in particular it appears that the experimental uncertainties have not always been fully appreciated. As an example it is only necessary to cite ethane, where an observed CC distance of 1·543 Å has long held the status of an absolute standard for the paraffinic CC bond. While many authors have taken this value to be accurate to 0·001 Å, improved measurements during the last three years have shown the correct distance to be 0·010–0·020 Å shorter. Furthermore, the precision of measurement of this and many other bond distances is now sufficiently high that it is necessary to consider the operational definition of the distance obtained by each experimental technique.

While ambiguities of 0·01–0·02 Å are small in an absolute sense, they are not much smaller than some of the bond-length variations which are regarded as theoretically significant. In this paper we shall discuss some of the difficulties in comparing carbon–carbon distances and afterwards review the status of measurements on different types of CC bonds. Some implications of the present measurements will also be pointed out.

THE MEANING OF MEASURED BOND LENGTHS

An ideal measurement of a bond length would provide a value for r_e, the distance between the two nuclei in the hypothetical vibrationless state of the free molecule. Any practical measurement, of course, will yield a distance which is averaged over the vibrational motion of the nuclei. It is clear that the nature of this averaging is not identical for the two principal methods of measurement, spectroscopy and electron diffraction. With sufficient knowledge of the vibrational motion we might hope

ultimately to be able to correct the average distances determined by each method to equilibrium values. While some progress is being made in this direction, we are at present unable to make this correction with confidence for any but the very simplest molecules. It is therefore important to examine the validity of comparing experimental bond lengths determined in different ways.

An analysis of the rotational spectrum of a molecule yields the three rotational constants a_0, b_0, c_0 for the ground vibrational and electronic state. It is customary to define ground-state moments of inertia as the reciprocals of these constants, viz., $I_a^0 = h^2/2a_0$, etc. It is well known that I_a^0 differs in a very complicated way from I_a^e, the moment calculated from the equilibrium co-ordinates r_e; since the rotational constants include a contribution from Coriolis interactions with excited states, it is not in general possible to express I_a^0 as an explicit average over the vibrational co-ordinates. In only a few cases, outside of diatomic molecules, is there enough information available to obtain accurate values of the I^e's. Consequently, most structures determined by spectroscopic methods have been of the so-called r_0 type. We may define an r_0 structure as a set of geometric parameters which reproduce the observed values of I_a^0, I_b^0, I_c^0 for the molecule. Such a structure is uniquely defined for diatomic molecules and for a few special polyatomic types such as linear XY_2 and tetrahedral XY_4 molecules. However, when we advance to the slightly more complicated case of a bent XY_2 molecule, the r_0 structure is no longer unique, since one can calculate three structures from the moments of inertia which will not be identical because of the finite inertial defect. When the number of independent structural parameters exceeds three, we must use the ground-state moments of more than one isotopic species (or else assume some of the parameters) in order to obtain the r_0 structure. Since the change of mass affects the vibrational motion as well, the resulting structure will depend upon our choice of isotopic species—a choice which in practice has often been dictated by natural isotopic abundances or the ease of chemical synthesis. Numerous examples have been given of r_0 structures which vary over a range of 0·01–0·02 Å when different combinations of isotopic species are used in the calculation. To reduce this problem, many investigators have studied more isotopic species than necessary and used a least squares procedure to obtain the "best" structure. However, the result is still dependent on the choice of imput data, and it is always difficult to assess the real uncertainties in such a structure.

We must conclude, then, that the r_0 structure is a rather fuzzily defined concept. This does not imply that r_0 structures are useless; indeed, in simple molecules the distance between heavy atoms is often relatively insensitive to the choice of data for the calculation. However, the lack of an unambiguous operational definition, and the consequent difficulty in estimating the probable errors, makes r_0 structures fundamentally unsuitable for the detection of small differences in bond distances. In an effort to avoid these problems Costain[1] has proposed the use of r_s or "substitution" structures. The r_s co-ordinates of a given atom in a molecule are determined by the isotope *shifts* in the moments of inertia when that atom (and no others) is substituted. A complete r_s structure thus requires single isotopic substitutions on every atom. The r_s parameters will not reproduce the ground-state moments I_a^0, I_b^0, I_c^0, but generally give calculated moments which are smaller. From this and other arguments Costain[1] has shown that the r_s parameters usually provide a closer approximation to the r_e's

[1] C. C. Costain, *J. Chem. Phys.* **29**, 864 (1958).

VOL. 17 1962

than do the r_0's. The exact relation between r_s and r_e is not yet understood for polyatomic molecules. However, the important advantage of the r_s structure lies in its unambiguous operational definition, which can be demonstrated by two tests: (1) in overdetermined systems different species may be used as the starting point for the isotopic substitutions, and the resulting r_s co-ordinates generally agree to 0·001 Å or better; (2) in molecules which have an axis or plane of symmetry one obtains essentially the same r_s parameters (at least for heavy atoms)[2] regardless of what combination of moments is used.[3] The most serious difficulty occurs when an atom is close to a principal inertial axis; in such a case the r_s co-ordinate is unreliable because of vibrational effects, and some other technique must be used. However, if we exclude these unfavorable examples (which are easily recognized), the self-consistency of r_s bond lengths to a precision of 0·001–0·002 Å or better has been demonstrated in a variety of molecules. We can therefore have considerably more confidence in comparing bond lengths in a series of molecules when they are all determined by the substitution method.

Interatomic distances measured by electron diffraction are generally reported either as r_m values, obtained from the maxima in the radial distribution curve, or r_g values, which are based on the centers of gravity of the peaks in the curve. The importance of specifying the type of distance which is reported has been emphasized by Bartell[4]. There is some evidence to indicate that r_g distances, at least when measured in the same laboratory, are suitable for precise comparison of bond lengths. For example, the CC distances in the normal hydrocarbons from butane through heptane,[5] where there is no reason to expect any significant difference in r_e values, fall in the range 1·531–1·534 Å (with a stated experimental uncertainty of 0·002 Å). However, an independent value of 1·539 ± 0·002 Å has also been reported for n-butane.[6]

If we tentatively accept that the electron-diffraction r_g distances provide a self-consistent set of bond lengths which may be compared among themselves, there remains the problem of their relation to the spectroscopic r_s distances. Unfortunately, there are not many examples where an accurate comparison can be made. In the case of saturated hydrocarbons, the r_s carbon–carbon distances in propane[7] and isobutane[8] are 1·526 ± 0·002 Å. Only an r_0 distance is available for ethane, but a rough correction[8] suggests that the r_s distance is in the range 1·525–1·530 Å. The r_g distance in the higher paraffins[5] is 1·533 ± 0·002 Å (with an alternative value of 1·539 Å), and 1·538 Å has been reported for ethane.[9] Therefore, it appears that r_g values for the CC distance are larger than the r_s values by something like 0·005–0·010 Å. Similarly, the r_g CH distances in the higher paraffins (an average of methyl and methylene groups) range from 1·108 to 1·121 Å, while in propane the methylene CH bond has an r_s length of 1·096 ± 0·002 Å, and the methyl CH bond is even shorter. There seems little doubt that these differences are outside the experimental precision of the respective methods.

[2] This is not always true for hydrogen atoms. There is particular difficulty when an atom is involved in a large-amplitude vibration, e.g. the torsional motion of a methyl group (see ref. 7).

[3] This means, for example, that the relation $\Delta I_a^\circ + \Delta I_b^\circ - \Delta I_c^\circ = 0$ is usually satisfied to a good approximation when an isotopic substitution is made in a planar molecule, while $I_a^\circ + I_b^\circ - I_c^\circ \neq 0$ because of zero-point vibrational effects.

[4] L. S. Bartell, *J. Chem. Phys.* **23**, 1219 (1955).

[5] R. A. Bonham, L. S. Bartell and D. A. Kohl, *J. Amer. Chem. Soc.* **81**, 4765 (1959).

[6] K. Kuchitsu, *Bull. Chem. Soc. Japan* **32**, 748 (1959).

[7] D. R. Lide *J. Chem. Phys.* **33**, 1514 (1960).

[8] D. R. Lide, *J. Chem. Phys.* **33**, 1519 (1960).

[9] A. Almenningen and O. Bastiansen, *Acta. Chem. Scand.* **9**, 815 (1955); corrected to an r_g value in ref. 5.

At the present time, then, several distinct types of bond distances are being reported, and these may differ from each other by considerably more than the strictly experimental uncertainties. Until it is possible to reduce these distances to some common denominator (preferably r_e) without too great a loss of accuracy, it is desirable to restrict oneself to a single type when comparing bond distances in different molecules. Even here, of course, one is tacitly assuming that r_s (or r_g, as the case may be) bears some constant relation to r_e; i.e. that the vibrational pattern does not differ markedly from one molecule to another. This is probably not too bad an assumption in the case of hydrocarbons, although its effect on methyl-group structures might be important.

With these problems in mind, we shall attempt a critical survey of the experimental results on the lengths of CC bonds of various types. Aromatic compounds will not be discussed because of the limited amount of data. Most of the comparisons will be made among r_s values, but r_g distances will be quoted when available.

C=C AND C≡C BONDS

There is now complete agreement that the C=C distance in ethylene, regardless of the method of measurement, is about 0·02 Å shorter than the 1·353 Å value which has been accepted for many years. Spectroscopic r_0 values of 1·337 ± 0·003 Å (infrared)[10] and 1·339 ± 0·003 Å (rotational Raman)[11] have been recently reported. We can estimate that the r_s distance is probably 1·330–1·335 Å; it is very unlikely to be less than 1·330 Å. Some reported r_s values in ethylene derivatives are 1·336 ± 0·004 Å in propylene,[12] 1·332 ± 0·002 Å in vinyl chloride,[13] 1·329 ± 0·006 Å in vinyl fluoride,[14] 1·325 ± 0·002 Å in 1,2-difluoroethylene,[15] 1·339 Å in vinyl cyanide[16] and 1·347 ± 0·003 Å in vinyl silane.[17] There appears to be a tendency for halogen substitution to decrease the C=C distance slightly,[15] and the vinyl silane distance is higher than the other examples; otherwise, the variations among these compounds are probably not significant. We can adopt 1·335 ± 0·010 Å as the characteristic r_s value for the C=C distance.

The constancy of the C=C distance is also supported by electron diffraction results. Some reported values are 1·333 ± 0·002 Å in ethylene,[18] 1·331 ± 0·003 Å in isobutylene[19] and 1·337 ± 0·005 Å in 1,3-butadiene.[20]

The r_s length of the C≡C triple bond has been accurately determined in methyl acetylene[1] (1·206 Å) and cyanoacetylene[1] (1·205 Å). The precision of these values should be about 0·001 Å. A somewhat less accurate value of 1·209 Å has been reported for propynal,[21] HC≡CCHO. In acetylene[22] itself r_0 = 1·207 Å and r_s = 1·205 Å. The constancy of the C≡C bond length at about 1·206 Å is therefore well-established.

[10] H. C. Allen and E. K. Plyler, *J. Amer. Chem. Soc.* **80**, 2673 (1958).
[11] J. M. Dowling and B. P. Stoicheff, *Canad. J. Phys.* **37**, 703 (1959).
[12] D. R. Lide and D. Christensen, *J. Chem. Phys.* to be published.
[13] D. Kivelson, E. B. Wilson and D. R. Lide, Jr., *J. Chem. Phys.* **32**, 205 (1960).
[14] Calculated from data of B. Bak, D. Christensen, L. Hansen-Nygaard and J. Rastrup-Andersen, *Spectrochim. Acta* **13**, 120 (1958); H. W. Morgan and J. H. Goldstein *J. Chem. Phys.* **30**, 1025 (1959).
[15] V. W. Laurie, *J. Chem. Phys.* **34**, 291 (1961).
[16] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* **30**, 777 (1959).
[17] J. M. O'Reilly and L. Pierce, *J. Chem. Phys.* **34**, 1176 (1961).
[18] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* **31**, 400 (1959).
[19] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* **32**, 824 (1960).
[20] A. Almenningen, O. Bastiansen and M. Trætteberg, *Acta Chem. Scand.* **12**, 1221 (1958).
[21] C. C. Costain and J. R. Morton, *J. Chem. Phys.* **31**, 389 (1959).
[22] J. H. Callomon and B. P. Stoicheff, *Canad. J. Phys.* **35**, 373 (1957).

The most accurate measurements available at this time indicate that any lengthening of double and triple bonds by conjugation must be extremely small—certainly less than 0·010 A and probably not over 0·005 Å. This result is consistent with most current theories. Even when conjugation is assumed to affect other molecular properties in an important way, recent calculations[23] indicate that multiple-bond lengthening should be the order of 0·005 Å or less.

C—C SINGLE BONDS

The near-constancy of the length of carbon–carbon single bonds of a given bond type has been pointed out many times.[16,24] We shall review the most recent measurements to see the extent to which this constancy is confirmed and to establish the best values for the various bond types. The symbols[23] *te*, *tr*, *di* will be used to indicate carbon atoms with hybridization sp^3, sp^2, *sp*, respectively. All distances are r_s values unless otherwise stated.

te–te. Two reliable r_s values are available for saturated hydrocarbons, 1·526 ± 0·002 Å in propane[7] and 1·525 ± 0·002 Å in isobutane.[8] It has already been mentioned that the estimated r_s distance in ethane is consistent with these. We shall adopt 1·526 ± 0·002 Å as the standard *te–te* distance.

te—tr. The best measurements of this bond length are 1·501 ± 0·004 Å in propylene,[12] 1·503 ± 0·003 Å in acetyl fluoride,[25] 1·490 ± 0·010 Å in acetyl cyanide,[26] and 1·500 ± 0·005 Å in acetaldehyde.[27] The acetaldehyde distance comes from an r_0 structure, but a recalculation shows that r_s probably does not differ by more than 0·005 Å. An r_0 distance of 1·507 Å has been found in isobutylene.[15] The agreement among these molecules is satisfactory, and it is reasonable to adopt a representative distance of 1·501 ± 0·004 Å.

The difference between the *te—te* and *te—tr* bond lengths is thus 0·025 Å, with an uncertainty of about 0·006 Å. The electron diffraction (r_g) result for the *te—tr* bond in isobutylene[19] is 1·505 ± 0·003 Å, which is 0·028 ± 0·005 Å shorter than r_g for the *te—te* bond.[5] This close agreement on the *difference* in bond lengths is encouraging. It has long been recognized that the *te—tr* bond is shorter, but previous estimates of the amount of this shortening were about twice as large as the present value.

te—di. Good determinations have been made[1] on methyl acetylene (1·459 Å) and methyl cyanide (1·458 Å). We may adopt a value of 1·459 ± 0·002 Å.

tr—tr. There is unfortunately no r_s value available for this bond type. A spectroscopic (r_0) structure has been reported for *s-trans* acrolein,[28] $H_2C{=}CH{-}CHO$; however, this structure is far from unique since only one isotopic species was studied. The reported C—C length of 1·45 Å is probably too low, since the C=C distance used (1·36 Å) is undoubtably too high. In 1,3-butadiene[20] the electron-diffraction value for the *tr—tr* distance is 1·483 ± 0·010 Å. One might *guess* that the r_s distance is 1·47 — 1·48 Å.

tr—di. Values of 1·426 Å in vinyl cyanide[16] and 1·447 Å in propynal[21] ($HC{\equiv}CCHO$) have been reported. Both distances are stated to be accurate to ± 0·001 Å. However, this appears to be somewhat optimistic, since one atom in each molecule is rather close

[23] R. S. Mulliken, *Tetrahedron* **6**, 68 (1959).
[24] G. Herzberg and B. P. Stoicheff, *Nature, Lond.* **175**, 79 (1955).
[25] L. Pierce and L. C. Krisher, *J. Chem. Phys.* **31**, 875 (1959)
[26] L. C. Krisher and E. B. Wilson, *J. Chem. Phys.* **31**, 882 (1959).
[27] R. W. Kilb, C. C. Lin and E. B. Wilson, *J. Chem. Phys.* **26**, 1695 (1957).
[28] R. Wagner, J. Fine, J. W. Simmons and J. H. Goldstein, *J. Chem. Phys.* **26**, 634 (1957).

to a principal axis. An uncertainty of about 0·004 Å is perhaps a more realistic estimate. Even so, there is no doubt that the bond length differs in the two molecules, and a still larger value, 1·466 ± 0·010 Å, has been obtained for acetyl cyanide.[26] Costain and Morton[21] have suggested that the replacement of $=CH_2$ by $=O$ tends to lengthen the adjacent C—C single bond by 0·02 Å; however, no such effect is noticed when propylene is compared with the acetyl compounds (see above). We cannot select a standard value for the *tr—di* bond length, but must accept a range from 1·42 to 1·46 Å.

di—di. Only one r_s value is available, 1·378 ± 0·001 Å in cyanoacetylene.[1] The r_0 length in diacetylene,[22] 1·376 ± 0·002 Å for an assumed C≡C length of 1·205 Å, is consistent with this.

TABLE 1. C—C SINGLE BOND LENGTHS (r_s VALUES)

Type	Obs. length[a] (Å)	Calculated length	
		Set A	Set B
te—te	1.526 ± 0·002	1·526	(1.526)[f]
te—tr	1.501 ± 0·004	1·506	(1·501)[f]
te—di	1·459 ± 0·002	1·454	(1·459)[f]
tr—tr	(~1·47 – 1.48)[b]	1·486	1·476
tr—di	1·426 ± 0·004[c] 1·445 ± 0·004[d] 1·466 ± 0·010[e]	1·434	1·434
di—di	1·378 ± 0·001	1·382	1·392
Radii:			
ρ_{te}		0·763	0·763
ρ_{tr}		0·743	0·738
ρ_{di}		0·691	0·696

[a] See text for molecules used.
[b] No r_s value available: estimate is based on electron diffraction result for 1,3-butadiene.
[c] Vinyl cyanide.
[d] Propynal.
[e] Acetyl cyanide.
[f] Used to calculate radii.

COVALENT RADII FOR CARBON

Several efforts have been made[29–31] to explain the characteristic lengths of the various C—C bond types in terms of a set of covalent radii which depend on the state of hybridization of the carbon atom. It is of interest to review this procedure in the light of the more accurate data now available. We wish to find three radii—ρ_{te}, ρ_{tr}, and ρ_{di}—which reproduce the characteristic lengths discussed in the last section (these are collected in Table 1 under "Obs. length"). The best overall fit is obtained with the radii listed under "Set A" in Table 1. With the exception of acetyl cyanide, which will be anomalous in any calculation, the mean deviation for this fit is 0·005 Å.

An alternative procedure is to assume that the bonds which involve a *te* carbon

[29] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959).
[30] G. R. Somayajulu, *J. Chem. Phys.* **31**, 919 (1959).
[31] H. J. Bernstein, *J. Phys. Chem.* **63**, 565 (1959).

VOL. 17 1962

atom can be characterized by a set of well-defined covalent radii—i.e. that hyperconjugation has a negligible effect on bond length. We can use the observed lengths of the *te*—*te*, *te*—*tr*, and *te*—*di* bonds to calculate these radii ("Set B" of Table 2) and then predict the remaining bond lengths. The *di*—*di* bond is seen to be 0·014 Å shorter than predicted, while for *tr*—*di* bonds, the distance in vinyl cyanide is 0·008 Å less, and that in propynal 0·011 Å greater (each $\pm$0·004 Å) than the predicted value. If we accept the electron-diffraction result on butadiene,[20] it is unlikely that the *tr*—*tr* bond, where we have no r_s value at present, differs very much from the predicted length of 1·476 Å. If we now wish to ascribe the differences between predicted and observed lengths to conjugation, its contribution need not be very large—roughly 10 per cent of the total shortening relative to the paraffinic bond is sufficient. Thus there is no contradiction with our premise that hyperconjugation is negligible. Furthermore, some other effect, perhaps electronegativity differences, of comparable importance to conjugation must be brought in to explain the observed variations in *tr*—*di* lengths.

The most accurate measurements available at this time confirm that the six C—C bond types can be "explained" with almost complete satisfaction by a set of three empirical radii. The interpretation of these radii is another matter. If we follow the ideas of Dewar and Schmeising[29], they may be regarded as characteristic covalent radii for carbon orbitals in different states of hybridization. The ratio of the differences $(\rho_{te} - \rho_{tr}):(\rho_{tr} - \rho_{di})$ is 0·025:0·042 with set B and 0·020:0·052 with set A. This agrees satisfactorily with the 1:2 ratio to be expected if one assumes that ρ is a linear function of the percentage of s character in the orbital.[29] A slightly more sophisticated calculation using expressions given by Coulson[32] predicts a ratio of 1:1·87. If one wishes to incorporate conjugation and polarity effects into this scheme in order to explain the slight deviations in Table 1, it is only *necessary* to treat them as minor factors whose contributions are of the order of 0·01 Å. Of course, it is possible that a larger contribution from electron-delocalization effects has been absorbed into the empirical radii. However, it seems less likely that a good fit in terms of empirical radii could be obtained if these resonance effects were the dominant factor, since they should be fairly sensitive to the molecular structure.

These conclusions are based upon the structures of a limited number of molecules, and they may have to be modified as more information becomes available. There is still a need for accurate measurements of CC bond lengths in a wide variety of compounds.

APPLICATION TO OTHER BONDS

It is natural to enquire whether the empirical radii derived in the last section permit any correlations of bond lengths involving carbon and another atom. Unfortunately, the reliable experimental data are somewhat limited, and it is necessary to mix bond lengths determined by different methods in order to make useful comparisons. Therefore, we cannot attach much significance to variations of less than 0·02 Å. We shall first survey the experimental results. Only bonds which are considered "single" in the zeroth approximation will be discussed.

Carbon–nitrogen bonds. Spectroscopic (r_0) values for *te* carbon are 1·474 Å in methylamine[33] and 1·472 $\pm$ 0·008 Å in trimethylamine.[34] The best example for *tr*

[32] C. A. Coulson, *Valence* p. 206. Oxford University Press, London (1953).
[33] D. R. Lide, *J. Chem. Phys.* **27**, 343 (1957).
[34] D. R. Lide and D. E. Mann, *J. Chem. Phys.* **28**, 572 (1958).

carbon is formamide, where two r_0 values, 1·343 Å[35] and 1·376 Å[36] have been reported. Further work will be necessary to establish a satisfactory structure for formamide, but we are probably safe in taking the C—N distance as 1·36 ± 0·02 Å. In cyanamide the N · · · N distance of 2·507 Å is well determined[37]; since C≡N distances are always close to 1·16 Å, we can adopt a value of 1·35 ± 0·02 Å for the *di* C—N distance.

Carbon–oxygen bonds. Some reported values for the *te* C—O bond are 1·427 ± 0·007 Å (r_0) in methyl alcohol,[38] 1·417 Å (r_0) in dimethyl ether,[39] and 1·437 ± 0·010 Å (r_s) in methyl formate.[40] The variation is probably not experimentally significant and we can take an average of 1·43 ± 0·01 Å. The most reliable determination of the *tr* C—O length in formic acid is 1·343 ± 0·010 Å (r_s),[41] and 1·334 ± 0·010 Å (r_s) has been reported for the similar bond in methyl formate.[40] Although some widely different values have been published for both formic and acetic acids, we feel that these are unreliable and that the correct distance is 1·34 ± 0·02 Å.

Carbon–fluorine bonds.[42] The r_s value for the *te* CF distance is 1·384 ± 0·001 Å in methyl fluoride.[1] The *tr* CF length is 1·347 ± 0·009 Å in vinyl fluoride[14] and 1·348 ± 0·015 Å in acetyl fluoride.[25] The distance in FC≡N and FC≡CH is in the range 1·26–1·28 Å.[43]

Carbon–chlorine bonds.[42] Accurate r_s values are available for methyl chloride[1] (1·781 ± 0·001 Å), vinyl chloride[13] (1·726 ± 0·002 Å) and cyanogen chloride[44] (1·631 ± 0·001 Å).

Carbon–silicon bonds. The bond length in mono-, di-, and tri-methyl silane[45] is 1·867 ± 0·002 Å (r_s), while that in vinyl silane[17] is 1·853 ± 0·003 Å (r_s). An r_s distance of 1·850 Å has been reported[46] for H_3SiCN.

The lengths of typical CX bonds, with X = N, O, F, Cl, and Si, are collected in the "Obs. r_{CX}" column of Table 2. The shortening of the *tr* and *di* bonds, relative to the bond to *te* carbon, is also listed. Now if the shortening observed for carbon–carbon single bonds is assumed to be due entirely to changes in the carbon hybridization, it is reasonable to transfer the reduction in carbon radius (0·025 Å for *tr* carbon and 0·067 Å for *di* carbon) to the CX bonds. The residual shortening of the CX bonds, after subtraction of this contribution from the carbon atom, is given in the last column of Table 2. A part of this residual shortening can be attributed to changes in hybridization of atom X; for example, the near-planar structure of formamide[35,36] and cyanamide[37] suggests that the nitrogen orbital contains a higher proportion of *s* character than in methylamine. However, it is difficult to ascribe the entire residual shortening (0·07–0·08 Å for CO and CN bonds) to hybridization changes, since the change from *te* to *tr* hybridization in carbon results in a shortening of only 0·025 Å. We therefore

[35] R. J. Kurland and E. B. Wilson, *J. Chem. Phys.* **27**, 585 (1957).
[36] C. C. Costain and J. M. Dowling, *J. Chem. Phys.* **32**, 158 (1960).
[37] J. K. Tyler, L. F. Thomas, and J. Sheridan, *Proc. Chem. Soc.* 155 (1959); D. J. Millen, G. Topping, and D. R. Lide, to be published.
[38] P. Venkateswarlu and W. Gordy, *J. Chem. Phys.* **23**, 1200 (1955).
[39] P. H. Kasai and R. J. Myers, *J. Chem. Phys.* **30**, 1096 (1959).
[40] R. F. Curl, *J. Chem. Phys.* **30**, 1529 (1959).
[41] G. H. Kwei and R. F. Curl, *J. Chem. Phys.* **32**, 1592 (1960).
[42] We shall consider only molecules with a single halogen atom because of the well-known tendency toward shorter bonds when several halogens are attached to the same carbon.
[43] J. Sheridan and J. K. Tyler, *Nature, Lond.* **185**, 96 (1960); *Proc. Chem. Soc.* 119 (1960).
[44] C. H. Townes, A.N.Holden, and F. R. Merritt, *Phys. Rev.* **74**, 1113 (1948).
[45] L. Pierce and D. H. Petersen, *J. Chem. Phys.* **33**, 907 (1960).
[46] Private communication from J. Sheridan; see also J. Sheridan and A. C. Turner, *Proc. Chem. Soc.* 21 (1960); N. Muller and R. C. Bracken, *J. Chem. Phys.* **32**, 1577 (1960).

VOL. 17 1962

have a strong argument for bringing in electron delocalization as a major factor in the shortening of the CX bonds.

There is no contradiction in the conclusion that delocalization contributes significantly to the shortening of CN, CO, CF, and CCl bonds but has a negligible effect on CC bond lengths. The N, O, F, and Cl atoms have lone pairs of electrons, and it is reasonable to expect that the transfer of charge form these lone-pair orbitals into a conjugated system involving a double or triple bond would greatly increase the

TABLE 2. CX BOND SHORTENING

X	C	Obs. r_{CX} (Å)	Bond shortening[a]	Residual shortening[b]
N	*te*	1·47 ± 0·01		
	tr	1·36 ± 0·02	0·11	0·08 ± 0.03
	di	1·35 ± 0·02	0·12	0·05 ± 0·03
O	*te*	1·43 ± 0·01		
	tr	1·34 ± 0·02	0·09	0·07 ± 0·03
F	*te*	1·384 ± 0·001		
	tr	1·347 ± 0·01	0·037	0·01 ± 0·01
	di	1·27 ± 0·01	0·11	0·05 ± 0·01
Cl	*te*	1·781 ± 0·001		
	tr	1·726 ± 0·002	0·055	0·030 ± 0·003
	di	1·631 ± 0·001	0·150	0·083 ± 0·002
Si	*te*	1·867 ± 0·002		
	tr	1·853 ± 0·003	0·014	−0·011 ± 0·005
	di	1·850	0·017	−0·050

[a] Relative to *te* CX bond.
[b] After correction for change in carbon hydridization.

stability of the molecule. The situation is quite different when there are two multiple bonds, as in 1,3-butadiene, since the electrons which are involved in the delocalization must come from an already existing bond. Actually, there is other evidence to show that the amount of delocalization is much greater in molecules containing lone pairs adjacent to a multiple bond. For example, the barriers to internal rotation about the CO bond in formic acid and the CN bond in formamide are very much higher than the barriers found in hydrocarbons; furthermore, the nuclear quadrupole coupling constants in vinyl chloride indicate a significant deviation from axial symmetry in the CCl bond, while no such effect is found in ethyl chloride.

It is interesting to note that the residual shortening of a CN bond is roughly the same for *tr* and *di* carbon. This is to be expected, since the NH_2 group provides only one lone pair to participate in the conjugated system. With halogen atoms, on the other hand, a much greater shortening occurs for *di* carbon, evidently because there are now two lone pairs to conjugate with the two π orbitals of the triple bond. In the case of silicon, where no lone pairs are available, there is a slight residual *lengthening* of the CSi bond, which indicates that delocalization is again a minor factor.

We have proposed a picture in which the length of a CC single bond is determined almost entirely by the hybridization of the carbon atoms, while electron delocalization effects have a strong influence on bond lengths in systems containing lone pairs. This appears to be the simplest scheme for explaining the observed bond-length variations, but no claim of uniqueness can be made. Some important factors have been omitted,

such as the influence of an adjacent bond involving an atom of high electronegativity.[47] However, the comparisons have been made in such a way as to minimize these effects. It should be emphasized that these statements about the importance of electron delocalization refer only to its effect on bond length. It is fairly obvious that certain other molecular properties (e.g. dipole moments) are much more sensitive to conjugation and hyperconjugation.

BOND ANGLES AND HYBRIDIZATION

In the derivation of covalent radii for carbon only the simple hybridization types sp, sp^2, and sp^3 were considered, although intermediate degrees of hybridization are certainly possible. The only objective measure of hybridization which has been proposed is based on bond angles.[48] It is instructive to calculate the value of λ, in the expression $s + \lambda p$ for the hybrid wave function, from the observed bond angles in some of the molecules for which good r_s structures are available. Table 3 gives the results for the C—C single bond in several related molecules; λ_m refers to the orbital of the methyl carbon and λ_o to the other carbon atom involved in the bond. The value of the

TABLE 3. HYBRIDIZATION PARAMETERS FOR C—C BONDS

Molecule	λ_m	λ_o	$(\lambda_m \lambda_o)^{1/2}$	r_{CC} (Å)
Propane	1·46	1·62	1·54	1·526 ± 0·002
Isobutane	1·74	1·66	1·70	1·525 ± 0·002
Propylene	1·52	1·38	1·45	1·501 ± 0·004
Acetaldehyde	1·58	1·36	1·46	1·500 ± 0·005
Acetyl fluoride	1·62	1·56	1·59	1·503 ± 0·003
Acetyl cyanide	1·64	1·48	1·56	1·490 ± 0·010

geometric mean $\sqrt{\lambda_m \lambda_o}$ is also given; this will equal 1·73 for a pure *te*—*te* bond and 1·56 for a pure *te*—*tr* bond. It is seen that the correlation between observed bond length and the value of $\sqrt{\lambda_m \lambda_o}$ is very poor —much poorer than we obtained by assuming the orbitals to be pure *te* or *tr*. Therefore, if we assert that hybridization has an important influence on the C—C bond length, we must conclude that bond angles do not provide a reliable measure of the hybridization.

The difficulty of using bond angles in this way can also be illustrated by calculating the hybridization of the carbon orbital which makes up the σ component of the double bond in ethylene derivatives. Values of λ range from 1·03 in CH_2CHF and CH_2CF_2 to 1·31 in ethylene itself—i.e. about $\frac{3}{4}$ of the way from a pure sp to a pure sp^2 orbital. If λ were a true measure of the hybridization, we should expect a much greater variation in the double-bond distance than is actually found. Many other examples have been cited where bond angles give a misleading or impossible estimate of hybridization. We can only conclude that other factors are generally of greater importance in determining the angles.

Acknowledgements—The author is indebted to the National Science Foundation for the award of a Senior Postdoctoral Fellowship and to the Chemical Laboratory of the University of Copenhagen for its hospitality during the preparation of this paper. Many helpful discussions with Professor Børge Bak are acknowledged.

[47] I. Lindqvist, *Nova Acta Regiae Societatis Scientiarum Upsalienis* (Ser. IV) Vol. 17, No. 11. Almqvist and Wiksells, Uppsala (1960).
[48] Ref. 32, pp. 194–196.

Tetrahedron 1962, Vol. 17, pp. 135 to 145. Pergamon Press, Ltd. Printed in Northern Ireland

THE VARIATION OF CARBON-CARBON BOND LENGTHS WITH ENVIRONMENT AS DETERMINED BY SPECTROSCOPIC STUDIES OF SIMPLE POLYATOMIC MOLECULES

B. P. STOICHEFF
Division of Pure Physics, National Research Council, Ottawa

VOL. 17 1962

(*Received* 13 *March* 1961)

Abstract—A brief and critical review of the spectroscopic method of determining molecular structures is given. The difficulties and present experimental accuracies of the method are discussed and comparisons with available diffraction values are made. Spectroscopic data on carbon–carbon bond lengths (accurate to 0·005 Å) which have been accumulated in recent years are summarized. These show a simple dependence on bond environment, namely, that bond lengths increase linearly with an increase in the number of adjacent bonds.

INTRODUCTION

RECENT developments in experimental techniques and in interpretation of experimental data have led to improved accuracy in the determination of molecular structure parameters by spectroscopic and diffraction studies. Thus at the present time bond lengths in simple molecules can be given to an accuracy of $\pm 0{\cdot}005$ Å or better. This accuracy has made it meaningful to assemble values of bond lengths in related molecules and justifies an attempt to derive relationships between bond lengths and various other bond properties.

A dependence of the CC single bond length on environment was first recognized by Herzberg, Patat and Verleger[1] in 1937. From an analysis of the photographic infra-red spectrum of methylacetylene, they showed that the C—C bond length in methylacetylene was 1·460 Å as compared to 1·540 Å for the C—C bond length in ethane. Further evidence of the variation of the CC single bond length was reported in 1939 by Pauling, Springall and Palmer[2] from their electron diffraction investigations.

A dependence of the CC double bond length on environment was first shown by Overend and Thompson[3] in 1953 from their study of the infra-red spectrum of allene. They found a C=C bond length of 1·30 Å in allene as compared with 1·34 Å in ethylene.

In recent years abundant data based on infra-red, microwave and Raman spectra as well as on electron diffraction experiments have been accumulated which confirm the variation of CC bond lengths with environment.[4,5] An analysis of these data has led to an empirical relation[5] for this dependence, namely, that the C—C, C=C and C—H bond lengths increase linearly with increase in the number of adjacent bonds (or adjacent atoms).

[1] G. Herzberg, F. Patat and H. Verleger, *J. Phys. Chem.* **41**, 123 (1937).
[2] L. Pauling, H. D. Springall and K. J. Palmer, *J. Amer. Chem. Soc.* **61**, 927 (1939).
[3] J. Overend and H. W. Thompson, *J. Opt. Soc. Amer.* **43**, 1065 (1953).
[4] G. Herzberg and B. P. Stoicheff, Nature, *Lond.* **175**, 79 (1955).
[5] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* **30**, 777 (1959).

It is the purpose of this paper to review very briefly the present status of experimental values of carbon–carbon bond lengths in simple polyatomic molecules. A summary is given of the most accurately known C—C, C═C and C≡C bond lengths determined from spectroscopic studies. An attempt is made to assess the deficiencies and accuracy of the spectroscopic method, and spectroscopic values of bond lengths are compared with available electron diffraction values. Finally, it is shown that the collected spectroscopic values confirm the simple relation, given above, of the dependence of carbon–carbon bond lengths on the number of adjacent bonds.

REVIEW OF THE SPECTROSCOPIC METHOD

In principle the spectroscopic method of determining molecular structures is simple and straightforward. From the molecular spectra (infra-red, microwave, Raman or electronic spectra) one obtains the rotational constants for a given vibrational state of the molecule under study. These are essentially reciprocals of the moments of inertia averaged over the vibrational state. When the rotational constants of a sufficient number of vibrational states are known it is possible to determine the constants for the equilibrium state (i.e. the minimum in the potential energy surface) and hence the equilibrium moments of inertia. The equilibrium structure can then be determined in two ways: (1) by solving a set of simultaneous equations of the moments of inertia for several isotopic species of the molecule,* the number of equations being equal to the number of unknown structural parameters,[6] or (2) alternatively, one can use the method described by Kraitchman[7] whereby the equilibrium position of each atom in a molecule is determined fromthe differences in the moments of inertia of two isotopic species of the molecule with the isotopic substitution being made for each atom in the molecule.† The two methods are entirely equivalent.

Following this brief discussion it may be well to emphasize several points about equilibrium structures. Firstly, molecular spectroscopy affords the only known means of determining equilibrium structures experimentally. Secondly, there is no ambiguity in the definition of equilibrium parameters and therefore the accuracy in evaluating these parameters is limited solely by experimental inaccuracies. With the best experimental techniques of today, equilibrium bond lengths can be given to $\pm 0{\cdot}001$ Å or better and bond angles to $\pm 15'$.

In practice, however, the experimental problems of obtaining such complete spectroscopic data for determining the equilibrium structures of polyatomic molecules are formidable. Up to the present time, the equilibrium structures of only the few polyatomic molecules listed in Table I have been reported.

On the other hand, spectroscopic data on the rotational constants for the ground vibrational states ($v_i = 0$) of molecules are more easily obtained, and values of these

* For all diatomic molecules and for linear symmetric triatomic molecules as well as for some simple asymmetric top molecules (as for example those listed in Table 1) only the constants of one molecular species are necessary to determine the complete structure.

† Since one can use the first moment equations in addition to the moment of inertia equations, the number of isotopic substitutions can be reduced.[7] The minimum number of substitutions is n-2 for linear and planar asymmetric top molecules and n-3 for non-planar asymmetric top molecules, where n is the number of atoms in the molecule.

[6] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* pp. 395, 434, 487. Van Nostrand, Princeton (1945).

[7] J. Kraitchman, *Amer. J. Phys.* **21**, 17 (1953).

VOL. 17 1962

constants are known for many polyatomic molecules. The ground state rotational constants give values of the "effective" moments of inertia or more precisely, they give average values of the reciprocals of the corresponding moments of inertia averaged over the zero-point vibrations.* It is the use of these "effective" moments of inertia that can lead to difficulties and sometimes to uncertainties in structure determinations.

The two methods for determining equilibrium structures, given above, can also be used for determining "effective" structures. In the first method one solves a set of simultaneous equations for the effective moments of inertia of several isotopic molecules and obtains the "effective" or "r_0" structure. However, a fundamental difference arises here: while it is expected that equilibrium internuclear distances (r_e) in isotopic molecules are the same (to better than $\pm$0·001 Å), it is known that effective internuclear distances (r_0) need not be exactly the same since the amplitudes of the zero-point vibrations are different in different isotopic molecules. The consequences of these "zero-point vibration effects" are well known.[6,8,9,10] One obtains slightly different "r_0" structures when solving equations for different sets of isotopic molecules,[8,10] the differences being largest when isotopic substitution has been made for an atom near a principal axis (within about 0·2 Å), or when the positions of hydrogen atoms are determined without deuterium substitution: also, ambiguities may arise because of the inertial defect for planar molecules[10] and because of analogous factors for non-planar molecules.[9]

Obviously we must discuss the question of just how much the "r_0" structures differ from the "r_e" structures. A comparison is made in Table 1 for all polyatomic molecules whose equilibrium structures are known. It is seen that the "r_0" values are no more than 0·005 Å larger than "r_e" and in most cases the differences are much less. (It may be mentioned here that this good agreement in "r_0" and "r_e" is found in all but a few of the known diatomic molecules. Of course, of necessity, one would not expect "r_0" and "r_e" to be the same in H_2, the lightest molecule, but even so they only differ by 0·009 Å.[11]) Unfortunately, only this limited comparison is possible at the present time for polyatomic molecules but the closeness of the "r_0" and "r_e" values shown here appears to confirm the belief of many spectroscopists that "r_0" structures are in fact very good approximations of the equilibrium structures.

Even better agreement with equilibrium structures is obtained by the second method of determining structures from ground state rotational constants. It is based on Kraitchman's equations[7] and the resulting effective structures are labelled "r_s" structures. Costain[10] has recently advocated this method and has given a detailed discussion of its advantages over the first method illustrated by several convincing examples. In this method one determines the co-ordinates (in the principal axis system) of each atom independently by making isotopic substitution for every atom in the molecule. In the calculations the differences of moments of inertia of two isotopic species are used and this results in a reduction of the zero-point vibration effects. It is found that the "r_s" structures are almost independent of the isotopic

* Any ground state rotational constant (for example B_0) is defined as $B_0 = \frac{h}{8\pi^2 c}\left(\frac{1}{I_B{}^0}\right)_{av.}$ see ref. 6, p. 461.

[6] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* p. 42. McGraw-Hill, New York (1955).
[8] V. W. Laurie, *J. Chem. Phys.* **28**, 704 (1958).
[10] C. C. Costain, *J. Chem. Phys.* **29**, 864 (1958).
[11] B. P. Stoicheff, *Canad. J. Phys.* **35**, 730 (1957).

species used to determine the structures: that is, the consistency of the "r_s" structures determined from different sets of isotopic species is within $\pm 0{\cdot}001$ Å.[10-12] Also, the errors in determing the co-ordinates of an atom are independent of the mass of the atom: therefore hydrogen atom positions are located with the same precision as positions of heavier atoms. As in the first method, errors may arise from the inertial defect or from substitution on atoms near a principal axis. In practice, the most reliable distances are those for atoms farther away than about 0·20 Å from principal axes. For atoms closer than 0·20 Å, the positions can be reliably determined by the use of the first moment equations if the positions of most of the other atoms have been determined: or when sufficient data are available, namely moments of inertia of doubly substituted atoms, one can use the second differences of the moments for locating "near-axis" atoms.[13] Other advantages are that partial structures may be determined by making isotopic substitutions only on atoms whose positions are required and that probable errors can be given for the co-ordinates of each atom. At present, isotopic substitution at each atom is not always feasible. In spite of this difficulty it is possible to determine "r_s" structures by microwave spectroscopy since its high sensitivity and high resolution permits the study of many isotopic molecules in their natural abundances. In infra-red and Raman spectroscopy, however, isotopic substitution is almost solely restricted to replacement of hydrogen by deuterium. A comparison of "r_s" and "r_e" structures is made in Table 1. It is seen that the "r_s" values are within $\pm 0{\cdot}003$ Å of the equilibrium values.

In conclusion, the present status of the spectroscopic method of determining molecular structures may be summarized as follows. The equilibrium structures of less than ten polyatomic molecules are known. Unfortunately, progress in this important field is slow and for a long time to come we shall have to be content with structure parameters obtained from ground state rotational constants. While the difficulties and limitations of such structure determinations are recognized there is considerable reason for optimism with the "r_s" and "r_0" structure parameters. The available data (Table 1) show that these parameters are the same as equilibrium parameters within 0·005 Å for bond lengths and 1° for bond angles, the "r_s" values being somewhat better than the "r_0" values. It is this closeness of "r_s" and "r_0" values to "r_e" values which now makes worthwhile the collection of bond lengths in related molecules in order to look for possible relations with bond properties.

COMPARISON OF SPECTROSCOPIC AND DIFFRACTION STRUCTURAL PARAMETERS

While the present paper is intended to deal primarily with spectroscopic structure determinations it is of interest to compare briefly the available diffraction and spectroscopic data. Such comparisons may be of importance in establishing possible differences in apparent structures determined by these two experimental methods. In Table 2 are listed the diffraction and spectroscopic values of structural parameters in several simple molecules. Only those values are included which were considered by the original investigators to be accurate to $\pm 0{\cdot}005$ Å and $\pm 1°$. Also, the results of as many investigators as possible are included in order to test the reproducibility of structure determinations.

[12] C. C. Costain and J. R. Morton, *J. Chem. Phys.* **31**, 389 (1959).
[13] L. Pierce, J. Mol. *Spectroscopy* **3**, 575 (1959); L. C. Krisher and L. Pierce, *J. Chem. Phys.* **32**, 1619 (1960).

VOL. 17 1962

It is seen that most of the values agree to within the experimental accuracy quoted above. Such good general agreement amongst the several different experimental techniques and amongst the various authors using the same technique is encouraging. Yet there are some significant differences which bear closer examination. For example, the diffraction values of the CH bond lengths in CH_4 (and CD_4) as well as in CH_3Cl are between 0·010 Å and 0·020 Å larger than the corresponding spectroscopic values and there is a discrepancy of about 2° in the values of the HCH angle in C_2H_4. These differences are several times the experimental errors given by the original investigators and appear to support the suggestion that there may be significant differences in the results of spectroscopic and diffraction structure determinations. Such differences may become more apparent as the accuracy of both techniques is improved and would be more conclusive if electron diffraction data for diatomic molecules were available for comparison with existing spectroscopic data. According to the results in Table 2, there appear to be small differences amongst different experimenters using the same methods, for example in the spectroscopic values obtained for the C—C bond length in ethane, and in the diffraction values of the C—C bond length in n-butane. Differences of this kind can only mean that further efforts are necessary by all investigators to adequately assess and to improve the accuracy of experimental values.

In spite of the generally good agreement shown in Table 2 between the diffraction and spectroscopic values of molecular structures, the main conclusions of this paper are based on spectroscopic results, not only because they are more plentiful but also for the sake of consistency. For the sake of completeness, however, the available electron diffraction values are included in the present compilation.

SUMMARY OF CARBON–CARBON BOND LENGTHS IN SIMPLE POLYATOMIC MOLECULES

The most extensive collection of CC bond lengths covering the period up to 1955 was published by Sutton *et al.*[14] in 1958. This collection includes all the CC bond lengths believed to be known to ±0·02 Å or better. Shorter compilations of values known more accurately have also been given:[4,5,15] one of these[5] includes only those values believed to be accurate to ±0·005 Å or better. The present collection of bond lengths forms an extension to the latter paper.

Tables 3 and 4 contain the CC bond lengths of all the gaseous polyatomic molecules for which accurate data are available. Table 3 includes open chain molecules and Table 4 cyclic molecules. The quoted bond lengths are considered to be the best values available at the present time. Most of the values are reported to be accurate to at least ±0·005 Å. A few values which are less accurate (to only ±0·01 Å) either because of larger experimental error or because they are not independent of some assumptions, have been included and are correspondingly labelled. As mentioned in the preceding section, most of the data have been obtained from molecular spectra, mainly from microwave spectra. The values are all "r_s" or "r_0" parameters determined from ground state rotational constants. Electron diffraction values (also reported to be accurate to ±0·005 Å or better) are included in Tables 3 and 4 to

[14] L. E. Sutton, D. G. Jenkin, A. D. Mitchell, L. C. Cross, H. J. M. Bowen, J. Donohue, O. Kennard, P. J. Wheatley and D. H. Whiffen, *Tables of Interatomic Distances and Configuration in Molecules and Ions*. The Chemical Society, London (1958).
[15] M. G. Brown, *Trans. Faraday Soc.* **55**, 694 (1959).

indicate their trend with changes in bond environment. A summary of CH bond lengths in simple polyatomic molecules is given in ref. 5.

DEPENDENCE OF CC BOND LENGTHS ON ENVIRONMENT

An examination of the bond lengths given in Table 3 confirms the conclusions of several recent investigations, namely, that the bond lengths for a given bond environment are remarkably constant in different molecules. This appears to be true even in the few examples where atoms of very different electronegativities are adjacent to the CC bonds. For the C≡C bond length, a small change is indicated when Cl, Br and F

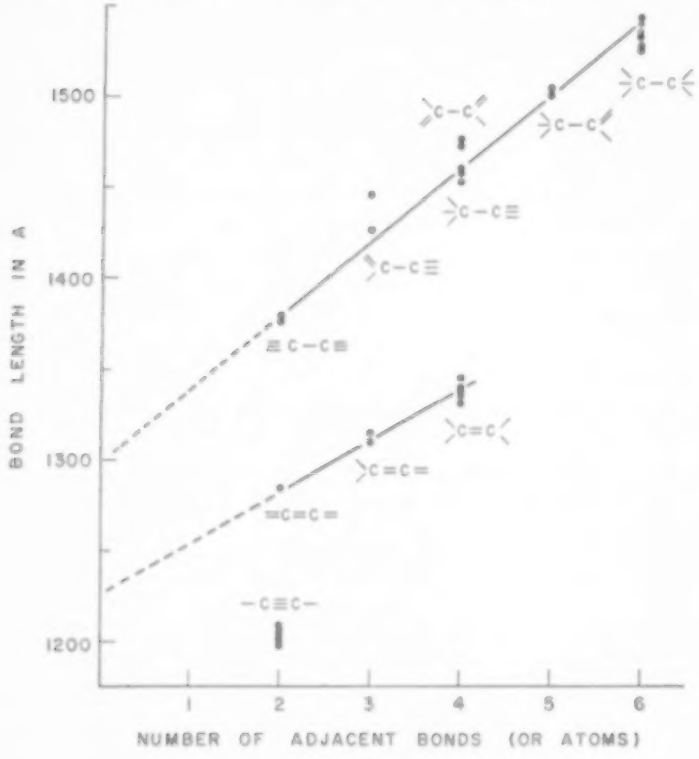


FIG. 1.

atoms are adjacent to the bond. But the scarcity of such data does not allow any conclusions to be drawn, at present, on the dependence of CC bond lengths on different adjacent atoms. The bond length data on ring compounds (Table 4) are also scanty and little can be said concerning a dependence on environment.

The data on C—C and C=C bond lengths confirm the earlier conclusions[4,5] that the bond lengths change systematically with the changes in bond environment: specifically, the bond lengths increase linearly with increase in the number of adjacent bonds (or adjacent atoms). These relationships are shown in the graphs of Fig. 1. Most of the values for the C—C bond lie within ±0·005 Å of a straight line given by the equation

$$r(\text{C—C}) = 1{\cdot}299 + 0{\cdot}040\,n \qquad n = 2, 3 \ldots 6$$

(where n is the number of adjacent bonds).

All the values for the C=C bond lie close to another straight line given by the equation

$$r(\text{C=C}) = 1{\cdot}226 + 0{\cdot}028\,n \qquad n = 2, 3, 4$$

Thus an analysis of the available spectroscopic data has given empirical relations for the average or "normal" behaviour of C—C and C=C (as well as C—H)[5] bond lengths.

There appear to be a few exceptions to this behaviour for the C—C bond. These include the values for butadiene, acrolein and propynal, the latter two being "r_s" values. The value given for butadiene is an "r_0" value but unfortunately is based on assumed ethylene parameters for the two CH=CH$_2$ groups. There is also, apparently, a rather wide range of values for the —C—C— bond length: these may be grouped into three values, 1·539 Å (r_0, ethane), 1·533 Å (r_s, ethyl fluoride) and 1·526 Å (r_s, propane, isobutane). The discrepancy between the ethane and propane–isobutane values appears to be too large to be accounted for by a difference in "r_s" and "r_0" values: one might perhaps expect a difference of at most 0·005 Å and hence an "r_s" ethane value of about 1·534 Å. A closer look at the isobutane structure determination shows that the off-axis C atoms are only 0·10 Å from the x–y plane (determined by C^{13} substitution) and their positions are subject to appreciable error, perhaps in the range of 0·010 to 0·020 Å. It is known that the "r_s" method errs in giving an apparent co-ordinate which is too small for "near-axis" atoms and thus it is possible that the C—C bond length in isobutane may be as large as 1·532 Å. The short C—C bond in propane is reminiscent of the short CH bond in methane,[5] the latter being approximately 0·01 Å shorter than the CH bonds in ethane, methyl acetylene and methyl cyanide.

No attempt has been made in this paper to explain the dependence of CC bonds on environment. Other authors have attempted to explain this dependence in terms of various descriptions of the carbon atoms and their environment. For example: Somayajulu[17] and notably Brown[15] and Dewar and Schmeising[16] discuss this dependence predominantly in terms of hybridization: Bernstein[18] in terms of π-bond orders; Mulliken[19] in terms of hybridization with appreciable contribution form conjugation and hyperconjugation; Bak and Nygaard[20] in terms of hybridization and electron delocalization; Wilmshurst[21] in terms of hybridization, bond order and ionicity; and Bartell[22] in terms of van der Waal's interactions between non-bonded atoms.

It is very difficult to test the validity or to determine the relative importance of these various concepts. This has not been the purpose of the present paper. Rather, the aim has been to establish experimentally the existence of a dependence of CC bond lengths on their environment.

I am grateful to Dr. G. Herzberg and Dr. C. C. Costain for many helpful discussions on this subject.

[16] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959); **11**, 96 (1960).
[17] G. R. Somayajulu, *J. Chem. Phys.* **31**, 919 (1959).
[18] H. J. Bernstein, *J. Phys. Chem.* **63**, 565 (1959).
[19] R. S. Mulliken, *Tetrahedron* **6**, 68 (1959).
[20] B. Bak and L. Hansen-Nygaard, *J. Chem. Phys.* **33**, 418 (1960).
[21] J. K. Wilmshurst, *J. Chem. Phys.* **33**, 813 (1960).
[22] L. S. Bartell, *J. Amer. Chem. Soc.* **81**, 3497 (1959).

TABLE I. COMPARISON OF EQUILIBRIUM AND GROUND STATE MOLECULAR STRUCTURES DETERMINED EXPERIMENTALLY BY SPECTROSCOPIC METHODS

Molecule	Parameters	r_e[a]	r_0	r_s	Ref.
CO_2	r(CO)	1·1600	1·162	1·1607	23
CS_2	r(CS)	1·5531	1·555	1·5525	24
HCN	r(CH)	1·0630	1·064	1·0632	10, 25
	r(CN)	1·1538	1·156	1·1554	
N_2O	r(NN)	1·126	1·129	1·1286	10
	r(NO)	1·186	1·191	1·1876	
H_2O	r(OH)	0·9572	0·963[b]	0·9609[b]	26
	∠(HOH)	104°31′	104°2′	103°33′	
D_2O	r(OD)	0·9575	0·962[b]	0·9615[b]	26
	∠(DOD)	104°29′	104°7′	104°21′	
NH_2	r(NH)	1·0124	1·017	1·0139[c]	27
	∠(HNH)	106°41′	107°47′	107°20′[c]	
ND_2	r(ND)	1·0108	1·016		27
	∠(DND)	106°42′	107°36′		
C_2H_2	r(CH)	1·0585	1·061		28, 29
	r(CC)	1·2047	1·207		

[a] All bond lengths are given in Å units.
[b] Average values obtained by taking I_A, I_B, I_C in pairs: if only I_A and I_B are used in the calculations the r_0 and r_s values are within 0·002 Å from the equilibrium values.
[c] The NH_2 and ND_2 values are necessary to obtain the "r_s" parameters.

[23] C. P. Courtoy, *Ann. Soc. Sci. Bruxelles* **73**, 5 (1959).
[24] A. H. Guenther and B. P. Stoicheff, *Canad. J. Phys.* to be published.
[25] J. W. Simmons, W. E. Anderson and W. Gordy, *Phys. Rev.* **86**, 1055 (1952).
[26] W. S. Benedict, N. Gailar and E. K. Plyler, *J. Chem. Phys.* **24**, 1139 (1956).
[27] W. S. Benedict and E. K. Plyler, *Canad. J. Phys.* **35**, 1235 (1957).
[28] M. T. Christensen, D. R. Eaton, B. A. Green and H. W. Thompson, *Proc. Roy. Soc.* A **238**, 15 (1956).
[29] J. H. Callomon and B. P. Stoicheff, *Canad. J. Phys.* **35**, 373 (1957).

VOL. 17 1962

TABLE 2. COMPARISON OF GROUND STATE MOLECULAR STRUCTURES DETERMINED EXPERIMENTALLY BY DIFFRACTION AND SPECTROSCOPIC METHODS

Molecule	Parameter	Diffraction value[a]	Spectroscopic value[b]
NH_3	r(NH)	1·016[30c]	1·0173 I[27]
ND_3	r(ND)	1·017[30]	1·0155 I[27]
CH_4	r(CH)	$1·107_0$[31]	1·0940 R[33] 1·0941 I[30]
CD_4	r(CD)	$1·102_2$[31]	$1·092_2$ R[34]
C_2H_4	r(CH)	1·084	1·086 I[36] 1·086 R[37]
	r(CC)	$1·332_7$	1·337 1·339
	<(HCH)	115°30′	117°22′ 117°34′
CH_3Cl	r(CH)	1·114[20]	1·096 M[10]
	r(CCl)	1·783	1·7812
C_2H_6	r(CH)	1·107[20]	1·102 I[40]
	r(CC)	1·536	1·543 1·534 I[41] 1·538 R[42]
C_3H_4	r(CC)	1·312[43]	1·309 R[44]
(Allene)	r(CH)	1·082	1·080 I[45]
C_6H_6	r(CC)	1·393[46] $1·39_2$[47] 1·397[48]	1·397 R[49]
	r(CH)	1·083	1·084
C_4H_{10}	r(CC)	1·533[50] 1·540[51]	
(*n*-butane)	r(CH)	1·108 1·100	

[a] All values have been obtained by electron diffraction experiments with gaseous molecules, the only exception being the CC bond length in benzene which was obtained by x-ray diffraction experiments with benzene crystals.

[b] The spectroscopic values have been obtained by means of infra-red (I) Raman (R) and microwave (M) spectra of gaseous molecules.

[c] The superscripts are reference numbers.

[30] A. Almenningen and O. Bastiansen, *Res. Correspondence* **9**, 35 (1956).
[31] L. S. Bartell, K. Kuchitsu and R. J. de Neui, *J. Chem. Phys.* **33**, 1254 (1960).
[33] M. A. Thomas and H. L. Welsh, *Canad. J. Phys.* **38**, 1291 (1960).
[33] K. T. Hecht, J. Mol. *Spectroscopy* **5**, 390 (1960).
[34] G. G. Shepherd and H. L. Welsh, *J. Mol. Spectroscopy* **1**, 277 (1957).
[35] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* **31**, 400 (1959).
[36] H. C. Allen and E. K. Plyler, *J. Amer. Chem. Soc.* **80**, 2673 (1958).
[37] J. M. Dowling and B. P. Stoicheff, *Canad. J. Phys.* **37**, 703 (1959).
[38] L. S. Bartell and L. O. Brockway, *J. Chem. Phys.* **23**, 1860 (1955).
[39] A. Almenningen and O. Bastiansen, *Acta Chem. Scand.* **9**, 815 (1955).
[40] G. E. Hansen and D. M. Dennison, *J. Chem. Phys.* **20**, 313 (1952).
[41] H. C. Allen and E. K. Plyler, *J. Chem. Phys.* **31**, 1062 (1959).
[42] B. P. Stoicheff, *Canad. J. Phys.* to be published.
[43] A. Almenningen, O. Bastiansen and M. Trætteberg, *Acta Chem. Scand.* **13**, 1699 (1959).
[44] B. P. Stoicheff, *Canad. J. Phys.* **33**, 811 (1955).
[45] D. R. Eaton and H. W. Thompson, *Proc. Roy. Soc.* A **247**, 39 (1959).
[46] I. L. Karle, *J. Chem. Phys.* **20**, 65 (1952).
[47] E. G. Cox, D. W. J. Cruickshank and J. A. S. Smith, *Proc. Roy. Soc.* A **247**, 1 (1958).
[48] A. Almenningen, O. Bastiansen and L. Fernholt, *Kgl. Norske Vid. Selsk. Skr.* No. 3 (1958).
[49] A. Langseth and B. P. Stoicheff, *Canad. J. Phys.* **34**, 350 (1956).
[50] R. A. Bonham and L. S. Bartell, *J. Amer. Chem. Soc.* **81**, 3491 (1959).
[51] K. Kuchitsu, *Bull. Chem. Soc. Japan* **32**, 748 (1959).

TABLE 3. A SUMMARY OF CC BOND LENGTHS IN OPEN CHAIN MOLECULES

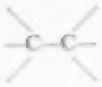
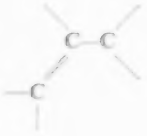
Bond type	Length[a]	Molecule	Reference[b]
	1·543	ethane C_2H_6	I, 40
	1·538	ethane C_2H_6	R, 42
	1·534	ethane C_2H_6	I, 41
	1·533	ethyl fluoride CH_3CH_2F	M, 52
	1·526	propane $CH_3CH_2CH_3$	M, 53
	1·525	isobutane $(CH_3)_2CH$	M, 54
	1·540	n-butane C_4H_{10}	ED, 51
	1·536	ethane C_2H_6	ED, 39
	1·534	n-heptane C_7H_{16}	ED, 55
	1·533	n-hexane C_6H_{14}	ED, 55
	1·533	n-butane C_4H_{10}	ED, 50
	1·531	n-pentane C_5H_{12}	ED, 55
	1·503	acetyl fluoride CH_3CFO	M, 56
	1·501	propylene CH_3CHCH_2	M, 57
	1·501	acetaldehyde CH_3CHO	M, 58
	1·505	isobutylene $(CH_3)_2CCH_2$	ED, 59
	1·476 ± 0·01[c]	butadiene $CH_2(CH)_2CH_2$	R, I, 60
	1·472	acrolein CH_2CHCHO	M, 61
	1·483 ± 0·01	butadiene	ED, 62
	1·459	methylacetylene CH_3CCH	M, 10
	1·458	methylbromoacetylene CH_3CCBr	M, 63
	1·458	methyl cyanide CH_3CCN	M, 10
	1·458	methylchloroacetylene CH_3CCCl	M, 64
	1·454	methylcyanoacetylene CH_3CCCN	M, 65
	1·445	propynal CHCCHO	M, 12
	1·426	vinyl cyanide CH_2CHCN	M, 5
	1·378	cyanoacetylene HCCCN	M, 10
	1·375	methylcyanoacetylene CH_3CCCN	M, 65
	1·344	acrolein CH_2CHCHO	M, 61
	1·339	ethylene C_2H_4	R, 37
	1·339	vinyl cyanide CH_2CHCN	M, 5
	1·337	ethylene C_2H_4	I, 36
	1·336	propylene CH_3CHCH_2	M, 57
	1·332	vinyl chloride CH_2CHCl	M, 66
	1·337	butadiene $CH_2(CH)_2CH_2$	ED, 62
	1·333	ethylene C_2H_4	ED, 35
	1·331	isobutylene $(CH_3)_2CCH_2$	ED, 59
	1·314	ketene CH_2CO	M, 67
	1·309	allene CH_2CCH_2	R, 44
	1·312	allene CH_2CCH_2	ED, 43
	1·284[c]	butatriene CH_2CCCH_2	R, 68
	1·280 ± 0·01	carbon suboxide C_3O_2	ED, 69, 70
	1·209	propynal CHCCHO	M, 12
	1·207	acetylene C_2H_2	I, R, 28, 29
	1·205	methylacetylene CH_3CCH	M, 10
	1·205	cyanoacetylene HCCCN	M, 10
	1·205	methylcyanoacetylene CH_3CCCN	M, 65
	1·204	chloroacetylene CHCCl	M, 63
	1·201	methylbromoacetylene CH_3CCBr	M, 63
	1·198	fluoroacetylene CHCF	M, 71

TABLE 4. A SUMMARY OF CC BOND LENGTHS IN CYCLIC MOLECULES

Bond type	Length[a]	Molecule	Reference[b]
	1·549	trimethylene oxide C_3H_6O	M, 72
	1·558	cyclobutane C_4H_8	R, 73
	1·515	cyclopropene $CH_2(CH)_2$	M, 74
	1·423	thiophene C_4H_4S	M, 76
	1·462	cyclooctatetraene C_8H_8	ED, 75
	1·397	benzene C_6H_6	R, 49
	1·394	pyridine C_5H_5N	M, 77
	1·397	benzene C_6H_6	ED, 48
	1·393	benzene C_6H_6	ED, 46
	1·370	thiophene C_4H_4S	M, 76
	1·300	cyclopropene $CH_2(CH)_2$	M, 74

Footnotes for Table 3 and 4.

[a] All bond lengths are in Å units (i.e. 10^{-8} cm)
[b] M = microwave, R = Raman, I = infra-red, ED = electron diffraction.
[c] In order to obtain these values some of the structural parameters were assumed.

[53] B. Bak, S. Detoni, L. Hansen-Nygaard, J. T. Nielsen and J. Rastrup-Andersen, *Spectrochim. Acta* **16**, 376 (1960).
[54] D. R. Lide, *J. Chem. Phys.* **33**, 1514 (1960).
[55] D. R. Lide, *J. Chem. Phys.* **33**, 1519 (1960).
[56] R. A. Bonham, L. S. Bartell and D. A. Kohl, *J. Amer. Chem. Soc.* **81**, 4765 (1959).
[57] L. Pierce and L. C. Krisher, *J. Chem. Phys.* **31**, 875 (1959).
[58] D. R. Lide and D. Christensen, *J. Chem. Phys.* to be published.
[59] R. W. Kilb, C. C. Lin and E. B. Wilson, *J. Chem. Phys.* **26**, 1695 (1957).
[60] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* **32**, 824 (1960).
[61] D. J. Marais, N. Sheppard and B. P. Stoicheff, *Tetrahedron* **17**, 163 (1962).
[62] C. C. Costain and E. Cherniak, Private communication (1961).
[63] A. Almenningen, O. Bastiansen and M. Trætteberg, *Acta Chem. Scand.* **12**, 1221 (1958).
[64] J. Sheridan, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1960.
[65] C. C. Costain, *J. Chem. Phys.* **23**, 2037 (1955).
[66] L. F. Thomas, J. S. Heeks and J. Sheridan, *Arch. Sci.* (*Geneva*) **10**, 18 (1957).
[67] D. Kivelson and E. B. Wilson, *J. Chem. Phys.* **32**, 205 (1960).
[68] A. P. Cox, L. F. Thomas and J. Sheridan, *Spectrochim. Acta* **15**, 542 (1959).
[69] B. P. Stoicheff, *Canad. J. Phys.* **35**, 837 (1957).
[70] O. Bastiansen, Private communication (1956).
[71] R. L. Livingston and C. N. R. Rao, *J. Amer. Chem. Soc.* **81**, 285 (1959).
[72] J. Sheridan, *Proc. Chem. Soc.* 119 (1960).
[73] S. I. Chan, J. Zinn and W. D. Gwinn, *J. Chem. Phys.* **34**, 1319 (1961).
[74] R. C. Lord and B. P. Stoicheff, to be published.
[75] P. H. Kasai, R. J. Myers, D. F. Eggers and K. B. Wiborg, *J. Chem. Phys.* **30**, 512 (1959).
[76] O. Bastiansen, L. Hedberg and K. Hedberg, *J. Chem. Phys.* **27**, 1311 (1957).
[77] B. Bak, D. Christensen, L. Hansen-Nygaard and J. Rastrup-Andersen, Private communication (1960). *J. Mol. Spectroscopy* **7**, 58 (1961).
[78] B. Bak, L. Hansen-Nygaard and J. Rastrup-Andersen, *J. Mol. Spectroscopy* **2**, 342 (1958).

VOL. 17 1962

VOL
17
196

Tetrahedron, 1962, Vol. 17, pp. 147 to 154. Pergamon Press, Ltd. Printed in Northern Ireland

THE NATURE OF BONDS BETWEEN CARBON ATOMS HOW THEY VARY WITH ENVIRONMENT

O. BASTIANSEN and M. TRÆTTEBERG
Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

VOL. 17 1962

(*Received* 16 *January* 1961)

INTRODUCTION

As a result of the incapability of quantum mechanics to yield an accurate and decisive solution for a system with a given number of nuclei and electrons, the whole theory of the chemical bond is based upon approximation calculations. These calculations have to a great extent been guided by experimental results, of which bond-length measurements and conformation studies have been of particular importance. The approximation approach has led to the introduction of a series of concepts that have often been introduced as a result of mathematical resignation. These concepts are therefore often merely of formal value and accordingly not of an obvious physical nature, though they are often referred to as "effects". Among these concepts some of the most important ones are hybridization, electron delocalization, resonance, conjugation, hyperconjugation, electronegativity, and steric effects.

Perhaps the most important characteristic of the chemical bond is the bond length. For the carbon–carbon bond the bond length does not vary much with the environment. It is often the case that a change in bond environment will lead to a bond distance effect which is less than the error limits of the experimental methods in use for bond length measurement. For the development of the theory of the chemical bond it is therefore of great importance to improve the experimental technique. It is also important to understand the principal differences of the results obtainable from the various methods. The safest procedure is to compare distances obtained using always the same experimental method.

The present contribution is nearly exclusively based upon results obtained by the Norwegian electron-diffraction group. It should be emphasized that all the molecules are studied in the vapour phase. The present authors would consider it too ambitious to try to cover more of the field than the very limited results of their own school. The field as a whole will no doubt be taken care of by the other contributors to this papers symposium.

Even when comparing results obtained from the same experimental method great difficulties arise as to the accuracy of the bond distance determinations. In the case of the electron-diffraction method for instance, the accuracy may be different for different compounds and also for different bonds in the same molecule. It is, therefore, very difficult to give a definite statement as to the accuracy. In favourable cases a bond distance can be reproduced to an accuracy of 0·001 Å. Reproducibility is, however, not the same thing as the absolute accuracy that depends upon scale factors and complicated definitions as to what a bond length actually means.

TABLE 1. C—C BOND DISTANCES OBTAINED FROM SPECTROSCOPIC METHODS AND FROM ELECTRON-DIFFRACTION

Type of bond	Bond distances in Å spectroscopic	Bond distances in Å electron diffraction
—C—C—	1·534[1]	1.536 ethane[2]
C—C	1·501[3]	
C—C	1·485[4]	1·483 1·3-butadiene[5] 1·462 cyclo-octatetraene[6]
—C—C	1·459	1·450 dimethyldiacetylene[7]
=C—C	1·426[8]	1·425 vinylacetylene[9]
=C—C=	1·377[10–12]	1·377 dimethyldiacetylene[7]
C=C	1·338	1·337 1·3—butadiene[5] 1·334 cyclo-octatetraene[6] 1·336 vinylacetylene[9]
=C=C	1·311[13,14]	1·312 allene[15] 1·318 butatriene[16]
—C=C—	1·284[17]	1·283 butatriene[16]
—C≡C—	1·207	1·207 vinylacetylene[9] 1·208 dimethyldiacetylene[7]

COVALENT RADII FOR CARBON

A number of hydrocarbons have been studied by the Norwegian electron-diffraction group. In Table 1 a series of C—C bond distances of non-aromatic open chain molecules have been listed and compared with distances obtained by spectroscopic methods. Some of the spectroscopic values are average values from several investigators. The general correspondence between the spectroscopically obtained values and the electron-diffraction values is satisfactory. The bonds have been grouped into

[1] H. C. Allen and E. K. Plyler, *J. Amer. Chem. Soc.* **31**, 1062 (1959).
[2] A. Almenningen and O. Bastiansen, *Acta. Chem. Scand.* **9**, 815 (1955).
[3] R. W. Kilb, C. C. Lin and E. B. Wilson, Jr., *J. Chem. Phys.* **26**, 1695 (1957).
[4] B. P. Stoicheff, Private communication (1959).
[5] A. Almenningen, O. Bastiansen and M. Trætteberg, *Acta Chem. Scand.* **12**, 1221 (1958).
[6] O. Bastiansen, L. Hedberg and K. Hedberg, *J. Chem. Phys.* **27**, 1311 (1957).
[7] A. Almenningen, O. Bastiansen and T. Munthe-Kaas, *Acta Chem. Scand.* **10**, 261 (1956).
[8] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* **30**, 777 (1959).
[9] T. Munthe-Kaas, Thesis, Oslo University (1955).
[10] J. H. Callomon and B. P. Stoicheff, *Canad. J. Phys.* **35**, 373 (1957).
[11] L. F. Thomas, J. S. Heeks and J. Sheridan, *Arch. Sci.* (*Genova*) **10**, 180 (1957).
[12] A. A. Westenberg and E. B. Wilson, Jr. *J. Amer. Chem. Soc.* **72**, 199 (1950).
[13] H. R. Johnson and M. N. P. Strandberg, *J. Chem. Phys.* **20**, 687 (1952).
[14] B. P. Stoicheff, *Canad. J. Phys.* **33**, 811 (1955).
[15] A. Almenningen, O. Bastiansen and M. Trætteberg, *Acta Chem. Scand.* **13**, 1699 (1959).
[16] A. Almenningen, O. Bastiansen and M. Trætteberg (unpublished).
[17] B. P. Stoicheff, *Canad. J. Phys.* **35**, 837 (1957).

the usual ten categories defined by the hybridization, six for the single bond, three for the double bond, and one for the triple bond. It seems to be of great importance to the theory of the C—C bond to extend this table to a larger number of molecules. An extended table would give valuable informations as to the relative importance of hybridization and bond delocalization. Without entering into the controversies on this point we shall make some comments from our data: The electron-diffraction bond lengths given in Table 1 form bases for calculating covalent radii for the carbon atom applicable for C—C bonds. The radii are given in Table 2. Of course the number of compounds presented in Table 1 is not sufficient to draw any far-reaching conclusion. On the other hand the given radii and a series of similar radii values published by other authors[8,18–20] indicate the usefulness of the kind of arguments leading to these values.

VOL. 17 1962

TABLE 2. COVALENT RADII OF THE C-ATOM FOR DIFFERENT TYPES OF HYBRIDIZATION

Bond multiplicity	C—	C=	C≡
sp^3	0·767		
sp^2	0·737	0·669	
sp	0·687	0·642	0·604

If one desires to argue in terms of σ-bonds and localized π-bonds some simple conclusions may be drawn. The bond shortening effect of a π-bond can for instance be studied. Comparing the three combinations sp^2sp^2, sp^2sp, and $spsp$, the bond shortening effect going from a single bond to the corresponding double bond is 0·137, 0·110 and 0·094 Å respectively. It is reasonable that the effect decreases with the length of the single bond to be contracted. In a similar way the effect of the first and second π-bond in an $spsp$ bond could be studied. The first π-bond contracts the total bond by an amount of 0·094 Å. The effect of the second bond is 0·076 Å. In Fig. 1 the bond shortening caused by one π-bond has been given as a function of the uncontracted distance. In this presentation the effect of the π-bond delocalization has of course been neglected, and this effect should according to the usual resonance theory be expected to be rather large.

THE sp^2–sp^2 C—C SINGLE BOND

For the study of resonance effects in terms of π-bond electron delocalization, the sp^2–sp^2 single bond is of particular interest. Two examples of such a bond are given in Table 1, namely for cyclo-octatetraene and for 1,3-butadiene. The bond distance is found to be 0·021 Å larger for 1,3-butadiene than for cyclo-octatetraene. This is a remarkable result in view of the fact that the 1,3-butadiene molecule is found to be a planar *trans* molecule while the bond arrangement around the single bond in cyclo-octatetraene is far from planar, the angle between the two planes being approximately 60°. This finding, if real, seems to be an important argument in the

[18] I. Hjalmars, *Acta Vålådalensia*. 29, (1958).
[19] B. Bak, *Acta Vålådalensia* 7 (1958).
[20] M. G. Brown, *Trans. Faraday Soc.* **55**, 694 (1959).

discussion of the influence of conjugation on the C—C single bond length. One must seek for arguments to explain the difference in the two distances as well as the fact that the 1,3-butadiene molecule is planar. If resonance does not result in a shortening of the central C—C bond distance, how could it then possibly be responsible for the planarity? A natural argument might be sought in the interaction between hydrogen atoms. One might for instance expect the hydrogen–hydrogen distances in the planar 1,3-butadiene molecule to be particularly favourable. However, a recent calculation

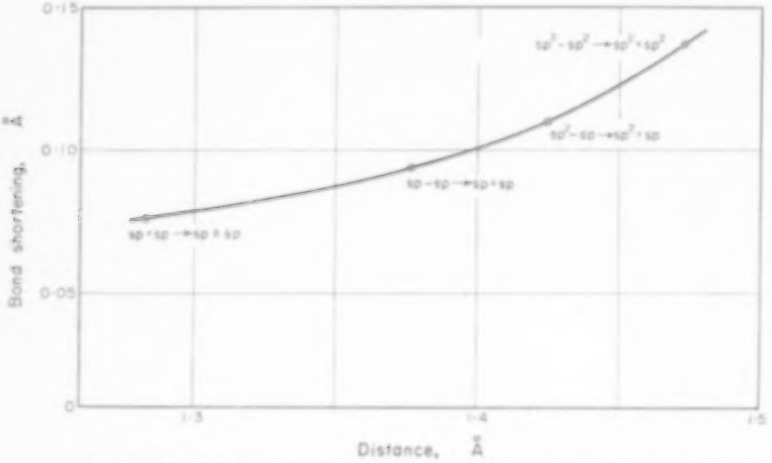


FIG. 1. Bond shortening caused by one π-bond as a function of the distance. (Values from the Norwegian electron diffraction work.)

carried out by Fischer-Hjalmars[21] does not seem to support this argument. According to her calculations, conjugation energy plays a more important part than the hydrogen–hydrogen interaction. If the dilemma is to be explained by resonance, the effect may perhaps be related to the cyclic form of cyclo-octatetraene that might favour the *p*-electron delocalization. One could of course question the reality of the effect. Though there are all reasons to believe that the effect is real, the authors feel in view of the importance of the problem that a simultaneous reinvestigation of cyclo-octatetraene and 1,3-butadiene should be carried through.

The sp^2–sp^2 single bond has been studied by the electron-diffraction method in a whole series of molecules where two aromatic rings are linked together. These molecules are, for example, biphenyl[22] and its derivatives,[23,24] bipyridyls,[22] sym-triphenylbenzene,[25] hexaphenylbenzene,[26] and 2,2′-dithienyl.[27] Unfortunately the bridge C—C bond distance in these molecules cannot be determined with particularly great accuracy by electron diffraction. The relative contribution of the bridge bond to the total electron scattering is small, and the distance has to be determined indirectly by studying larger internuclear distances between two different rings. Biphenyl itself is probably that of the above molecules for which the most accurate

[21] I. Fischer-Hjalmars, to be published.
[22] A. Almenningen and O. Bastiansen, *Kgl. Norske Vid. Selsk. Skr. No.* 4 (1958).
[23] O. Bastiansen, *Acta Chem. Scand.* **4**, 926 (1950).
[24] O. Bastiansen and L. Smedvik, *Acta Chem. Scand.* **8**, 1593 (1954).
[25] O. Bastiansen, *Acta Chem. Scand.* **6**, 205 (1952).
[26] A. Almenningen, O. Bastiansen and P. N. Skancke, *Acta Chem. Scand.* **12**, 1215 (1958).
[27] A. Almenningen, O. Bastiansen and P. Svendsås, *Acta Chem. Scand.* **12**, 1671 (1958).

distance value has been obtained. It was found to be 1·489 Å with a standard deviation of 0·0075 Å. The molecule seems to be far from rigid, and a rather large amplitude of rotational oscillation around the equilibrium position seems to exist. However, the electron-diffraction studies give a clear indication for a non-planar equilibrium conformation with an angle of 41·6° between the two phenyl rings. The deviation from planarity in the gaseous phase can easily be explained by interaction between hydrogen atoms. A comparison between the results of 1,3-butadiene and that of biphenyl also favours the idea that resonance seems to play a less important part for the bond distance. The two sp^2–sp^2 C—C distances are, within the error of the method, the same in spite of the less favourable angle arrangement for biphenyl.

VOL. 17 1962

For the other molecules containing aromatic rings linked together with single bonds the electron-diffraction studies carried out so far hardly give sufficiently accurate values for the bridge bond length to draw decisive conclusions. Altogether about 15 such molecules have been studied with results ranging from 1·47 to 1·52 Å. Some of these results have been obtained using older technique and are therefore less reliable. The only result beside biphenyl that might be accurate enough to be considered in this relation is that from hexaphenylbenzene. The sp^2–sp^2 C—C bond length was found to be 1·515 Å.[25] The estimated error limit is 0·015 Å. If this deviation from the biphenyl values is real, the longer distance might reasonably be related to the average 90° angle found between two directly linked rings.[21] The 1·515 Å distance should then correspond to an sp^2–sp^2 distance free of *p*-electron delocalization effects. Steric effects are of course of great importance for the conformation of the molecule, as interaction between hydrogen atoms no doubt is responsible for the 90° angle between each of the peripherical rings and the central ring. But also in the orthogonal conformation there are steric difficulties due to interaction between carbon atoms in neighbouring peripherical rings. This steric effect is, however, probably too small to contribute appreciably to the lengthening of the C—C bridge bond.

A systematic study of the angle between neighbouring rings in the biphenyl and bipyridyl group of molecules may throw some light on the resonance effect. For biphenyl and 4,4′-bipyridyl the deviation from planarity in the gaseous state is found to be as large as 42° and 37° respectively.[22] The resonance energy that should be gained in the planar form does not seem to be sufficient to overcome the repulsion between hydrogen atoms. A molecule of considerable interest in this connection is the 2,2′-bipyridyl molecule. In the *trans* form this molecule should be free from steric difficulties. One should, therefore, expect to find a pure *trans* molecule. This is not the case. The molecule does not seem to exhibit any well defined conformation. There seems to be a nearly free rotation through large angle intervals. The resonance energy does not seem to be large enough to keep the 2,2′-bipyridyl molecule in the sterically unhindered planar *trans* form. One might ask for the effect of the attractive force between the two hydrogen atoms in *ortho* position to the bridge bond. If this force were predominating, the molecule would have assumed an unplanar *cis* form corresponding to the most favourable H—H van der Waals' distance. Probably both the *trans* form and this unplanar *cis* form may correspond to energy minima, but the maxima in the energy curve given as a function of the angle, does not seem to be sufficiently high to favour any of the two stable conformations at the temperatures applied in the electron-diffraction experiment.

A group of molecules of interest in this connexion are the 2,2′-dihalobiphenyls.

Electron-diffraction studies lead to the surprising result that these molecules prefer a near *cis* instead of a near *trans* conformation. The inter planar angles found are 60°, 74°, 75° and 79° for the fluoro-, chloro-, bromo- and iodo-derivatives respectively. (Angle zero refers to the planar *cis* form.)[23,24] The conclusion to be drawn is that attractive van der Waals' forces of the London force type and not the repulsive dipole forces play the predominating part for these molecules. Conclusions along the same lines were obtained by Hampson and Weissberger from their dipole moment measurements.[28]

INFLUENCE OF NEGATIVE GROUPS

Of particular interest for our understanding of the influence of environment on the carbon–carbon bond are studies of molecules containing halogen atoms or other negative groups in the neighbouring position to the bond in question. Unfortunately the literature describing bond length measurements does not seem to form the basis for empirical rules. The present authors have made a list of approximately 50 molecules from the literature of the last few years without being able to discover any real systematical trends. There are many examples indicating bond length effects due to negative neighbour atoms but the results are often contradictory. For example, in hexafluoroethane indications are found for a somewhat larger C—C bond length than in ethane.[29] On the other hand recent work by Morino and Hirota[30] for hexachloroethane leads to a C—C bond distance considerably shorter than that of ethane. In the case of ethylene derivatives Morino *et al.*[31] have found a C—C bond distance in tetrafluoro- and 1,1′-difluoroethylene somewhat shorter than the ethylene distance, while microwave and infra-red work by Dowling[32] for 1,1′-dibromoethylene lead to a distance slightly larger than that of ethylene. It seems to be very difficult to find a single theory that can explain the various shortenings and lengthenings observed. The feeling of the present authors is that considerably more systematic experimental work should be carried out in this field before theoretical explanations are aimed at. It might be mentioned that preliminary results in this laboratory for 1,2-dichloroethane and 1,2-dibromoethane indicate a shortening of the C—C bond compared with that of ethane.[33] The observed shortening is, however, only 0·02 Å instead of the earlier reported shortening of 0·05 Å[34] for the chloro compound.

RINGS AND BENT BONDS

To study the influence of the so-called bent bonds it is important to measure the C—C bond lengths with the highest possible accuracy. The most important molecule in this connection is cyclopropane. Three independent electron-diffraction studies have been carried out on this molecule during the last few years. The structure parameters are: C—C distance 1·509 Å, C—H distance 1·091 Å, and HCH angle 113·8°. The estimated error limits are ±0·003 Å, ±0·01 Å and ±2° respectively.[35]

[28] G. C. Hampson and A. Weissberger, *J. Amer. Chem. Soc.* **58**, 211 (1936).
[29] D. A. Swick and I. L. Karle, *J. Chem. Phys.* **23**, 1499 (1955).
[30] Y. Morino and E. Hirota, *J. Chem. Phys.* **28**, 185 (1958).
[31] Y. Morino, K. Kuchitsu and T. Shimanouchi, *J. Chem. Phys.* **20**, 726 (1952).
[32] J. M. Dowling, *J. Chem. Phys.* **26**, 233 (1957).
[33] A. Almenningen, O. Bastiansen and J. Brunvoll, unpublished.
[34] L. E. Sutton, A. D. Mitchell, L. C. Cross, H. J. M. Bowen, J. Donohue, D. G. Jenkin, D. Kennard, P. J. Wheatley and D. H. Whiffen, *Tables of Interatomic Distances and Configuration in Molecules and Ions*. Chemical Society, London (1958).
[35] A. Almenningen, O. Bastiansen and P. N. Skancke, *Acta Chem. Scand.* In press.

For cyclobutane the best C—C and C—H distances obtained are 1·548 Å and 1·092 Å respectively.[36] The rather large C—C distance value is probably related to the repulsion between two carbon atoms in diagonal position. For cyclopentane a C—C distance of 1·539 Å is observed.[36] This is nearly the same as that observed for ethane.

Both the cyclobutane and cyclopentane molecule seem to deviate from the symmetric form with a four respectively fivefold axis of symmetry. This deviation seems to affect both the hydrogen atoms and the carbon atoms. Both molecules exhibit a non-planar carbon skeleton.

VOL. 17 1962

CONDENSED AROMATIC RING SYSTEMS

Electron-diffraction studies on naphthalene, anthracene, and coronene[37,38] have been carried out, and the results are compared with those obtained by Cruickshank *et al.* using X-ray crystallographic methods.[39] Really reliable values have been obtained only for naphthalene, and they correspond very satisfactorily with those obtained by Cruickshank *et al.* Naphthalene should, therefore, be a good case for testing various theoretical approaches.

It is interesting to note the increase in the average C—C bond distance with the size of the molecules. The average C—C bond distances found by electron-diffraction studies for benzene, naphthalene, anthracene, and coronene are: 1·397, 1·401, 1·408 and 1·415 Å respectively. One could include graphite in this list with its C—C bond distance of 1·421 Å. By comparing graphite with the aromatic molecules mentioned one should, however, keep in mind the principal difference that exists. In graphite *p* electrons no doubt play some part in keeping the layers in the lattice together. For the free molecules as studied in the vapour phase all the *p* electrons are engaged within the molecule.

FREE AND RESTRICTED ROTATION

The problem of free and restricted rotation around a C—C bond is no doubt greatly dependent upon the bond environment. A large amount of experimental work has been done in this field and review articles[40,41] and books[42] have been devoted to the problem. The problem was also partly discussed earlier in this article. The only question we want to raise in this connexion is the following: Do carbon–carbon bonds around which there is entirely free rotation exist at all? One could think of molecules of the type as butyne-2. The sp^3–sp C—C bonds at the two ends of the molecule should not lead to restriction and the central triple bond should according to well established views have cylinder symmetry. Further the distance between the two methyl groups should be so large that no appreciable steric effect should be expected. Electron-diffraction studies on 1,4-dibromobutyne-2[43] and 1,4-dichlorobutyne-2[44] have been carried out. No detectable restriction is observed. Electron-diffraction studies, however, can not exclude a possible existence of a small potential barrier of say 100–200 cal/mole.

[36] A. Almenningen, O. Bastiansen and P. N. Skancke, *Acta Chem. Scand.* In press.
[37] O. Bastiansen and P. N. Skancke, *Advanc. Chem. Phys.* In press.
[38] A. Almenningen, O. Bastiansen and F. Dyvik, *Acta Cryst.* In press.
[39] D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc. A* **258**, 270 (1960).
[40] S. Mizushima and T. Shimanouchi, *Ann. Rev. Phys. Chem.* **7**, 445 (1956).
[41] O. Bastiansen and E. W. Lund, *Ann. Rev. Phys. Chem.* **10**, 31 (1959).
[42] S. Mizushima, *Structure of Molecules and Internal Rotation.* Academic Press, New York, (1954).
[43] A. Almenningen, O. Bastiansen and F. Harshbarger, *Acta Chem. Scand.* **11**, 1059 (1957).
[44] K. Kuchitsu, *Bull. Chem. Soc. Japan* **30**, 399 (1957).

SOME CONCLUDING REMARKS

The present contribution has come out more as a series of statements on experimental results than a real discussion of the theoretical aspects involved. The authors have considered this as their main task.

In concluding, we want to emphasize again the errors that occur in any experimental result. Being among those who are putting out distance values and other structure parameters on the market for the use by theoreticians we feel particularly responsible on this point. It should be remembered that precision measurements of structure parameters are difficult to carry out, but it is still more difficult to give a realistic evaluation of the error limits. Calculation of standard deviations gives no doubt a good indication of the relative error in various distances in the same molecule, and the study of reproducibility gives a good indication of the reliability of the method. However, each molecule presents the investigator with new problems and every new experiment may be obscured by unexpected irregularities.

These warnings are hoped to help avoiding elaborate theoretical calculations to be based upon experimental effects of dubious existence. Unfortunately many of the most interesting effects from a theoretical point of view correspond to structural changes on the limit of the experimental methods.

Tetrahedron, 1962, Vol. 17, pp. 155 to 161. Pergamon Press, Ltd. Printed in Northern Ireland

X-RAY RESULTS ON AROMATIC HYDROCARBONS

D. W. J. CRUICKSHANK
School of Chemistry, The University, Leeds 2

(*Received* 13 *January* 1961)

Abstract—Recent X-ray results for the bond lengths in naphthalene and anthracene agree to about 0·01 Å with the simple MO and Pauling theories. Chrysene and quaterrylene are also discussed. The bearing of these results on the controversy about the effects of environment and π-bonding in CC bonds is considered.

VOL. 17 1962

1. INTRODUCTION

A NUMBER of recent discussions, particularly those of Stoicheff and his colleagues,[1,2] have shown how the measured CC bond lengths in hydrocarbons with unique classical structures all lie close to values characteristic of the environment of the bond. Thus when each carbon is three-co-ordinated any C—C single bond has a length of about 1·48 Å. Further the bond lengths alter regularly with the co-ordination numbers. The constancy of the bond lengths in particular environments suggests rather strongly that the unique classical structure has a high degree of relevance as a simple picture, so that the central bond in butadiene "really" has little or no π-bond character. This view has been argued[3,4] especially by Dewar and Schmeising.* On the other hand Mulliken[6] has argued that, though the simple Hückel theory leads to difficulties, up-to-date MO π-electron resonance theories are consistent with the constancies of the bond lengths in the particular environments. However, even though the more recent MO theories may drop the bond order for the central bond in butadiene to about 0·2, it remains a distinct difficulty to them that the observed length of 1·462 Å in the much-puckered cyclo-octatetraene[7] is less than the 1·483 Å in butadiene.[8] The results[9] for diphenyl and 2,2′-dipyridyl, which does not maintain the sterically unhindered planar *trans* form, also suggest very little π-character in their central C—C bonds.

The aromatic hydrocarbons do not have unique classical structures and their CC bonds must have partial double-bond character on any theory. Discarding benzene and graphite, in each of which all the bonds are of equal length and which all the theories are arranged to fit, the study of these molecules should be useful in the controversy over the relative effects of π-bonding and environment. In the six-membered rings all carbons are three-co-ordinated and, to the extent to which adjacent links to hydrogen or to carbon have the same effects, the environment of all CC bonds is the same. The variation of CC bond lengths within one molecule and in

* It is not important to this paper whether the change in carbon radius with environment is due to hybridization changes[3,4] or to the effects of intramolecular repulsions.[5]

[1] G. Herzberg and B. P. Stoicheff, *Nature, Lond.* **175**, 79 (1955).
[2] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* **30**, 777 (1959).
[3] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959).
[4] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **11**, 96 (1960).
[5] L. S. Bartell, *J. Chem. Phys.* **32**, 827 (1960).
[6] R. S. Mulliken, *Tetrahedron* **6**, 68 (1959).
[7] O. Bastiansen, L. Hedberg and K. Hedberg, *J. Chem. Phys.* **27**, 1311 (1957).
[8] A. Almenningen, O. Bastiansen and M. Traetteberg, *Acta Chem. Scand.* **12**, 1221 (1958).
[9] A. Almenningen and O. Bastiansen, *Det Kgl. Norske Vid. Selsk. Skrift.* No. 4 (1958).

different molecules is thus primarily a reflection of their different π-bond characters and may be used to test the merits of different valence theories without the complications of drastically changing environments. Some years ago it seemed that the experimental results were better fitted by MO theories than by any kind of VB theory, including the simplest Pauling-type theory of the resonance of classical structures. More recent and more accurate X-ray crystallographic results show that both the simple MO theory and the simple Pauling method predict CC lengths in sterically-unhindered aromatic molecules to within about 0·01 Å. Thus the resonating-classical-structures method does almost as well for aromatic molecules as the unique-classical-structure approach does for the non-aromatic hydrocarbons. The present paper discusses these problems in the light of four very recent papers on the crystal structures of aromatic molecules which appeared in *Proc. Roy. Soc.* (Ser. A) in September and October 1960. Cruickshank and Sparks[10] gave results for naphthalene and anthracene, Burns and Iball[11] for chrysene, Shrivastava and Speakman[12] for quaterrylene, and Mason[13] for 1·2:8·9-dibenzacridine. The paper by Cruickshank and Sparks also included a considerable discussion of the VB and MO theories and their predictions for all these molecules. The present paper, prepared by request for this Symposium and therefore written close on the heels of the Cruickshank and Sparks paper, is partly a summary of points made there and the reader is referred to it for a fuller discussion of many details.

2. NAPHTHALENE AND ANTHRACENE

The new experimental bond lengths for naphthalene and anthracene presented by Cruickshank and Sparks[10] are combinations of several independent refinements of sets of three-dimensional X-ray data. The results for naphthalene are the average of Cruickshank's refinement of the data of Robertson *et al.*[14] by the differential-synthesis method and Sparks' refinement of the same data by the least-squares method. The results for anthracene are a weighted average of the similar refinements of the data of Robertson *et al.* together with Sparks' least-squares refinement of Phillips' high-accuracy proportional-counter data. These refinements all allowed for the anisotropic vibrations of the atoms in the crystals and included corrections for finite series and peak overlapping effects, and also for the apparent atomic displacements caused by the rotational oscillations of the molecules.[15] The results of the various refinements were in satisfactory agreement. The final averaged bond lengths are given in Table 1. Their e.s.d's, estimated a little more conservatively than in some earlier work, are approximately 0·005 Å for naphthalene and 0·004 Å for anthracene. The present bond lengths have an r.m.s. difference of 0·016 Å from those found directly from the electron density maps without any corrections by Robertson and his colleagues, and have an r.m.s. difference of 0·011 Å from those given by Ahmed and Cruickshank[16] after application of simple finite series corrections. The successive corrections have brought

[10] D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.* A **258**, 270 (1960).
[11] D. M. Burns and J. C. Iball, *Proc. Roy. Soc.* A **257**, 491 (1960).
[12] H. N. Shrivastava and J. C. Speakman, *Proc. Roy. Soc.* A **257**, 477 (1960).
[13] R. Mason, *Proc. Roy. Soc.* A **258**, 302 (1960).
[14] napthalene: S. C. Abrahams, J. M. Robertson and J. G. White, *Acta Cryst.* **2**, 233, 238 (1949).
anthracene: A. McL. Mathieson, J. M. Robertson and V. C. Sinclair, *Acta Cryst.* **3**, 245 (1950); V. C. Sinclair, J. M. Robertson and A. McL. Mathieson, *Acta Cryst.* **3**, 251 (1950).
[15] D. W. J. Cruickshank, *Acta Cryst.* **9**, 757 (1956)
[16] F. R. Ahmed and D. W. J. Cruickshank, *Acta Cryst.* **5**, 852 (1952).

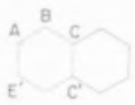
small increases in the mean bond lengths of each molecule, but some less regular changes have also occurred. In particular the difference between the corresponding internal bonds CC′ in naphthalene and CE′ in anthracene has been reduced from 0·045 Å in Robertson's results to 0·010 Å at present. This reduction has removed a source of much theoretical perplexity.

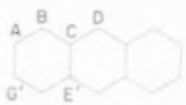
The new X-ray results are in remarkably good agreement with those obtained by Almenningen, Bastiansen and Dyvik[17] in their gas phase electron-diffraction study. The r.m.s. difference is only 0·004 Å, which seems fortuitously small.

VOL. 17 1962

TABLE 1. BOND LENGTHS (Å) IN NAPHTHALENE AND ANTHRACENE

Bond	Experimental	Pauling superposition	Simple MO
Naphthalene			
AB	1·364	1·375	1·384
BC	1·421	1·421	1·416
CC′	1·418	1·421	1·424
AE′	1·415	1·421	1·406
Anthracene			
AB	1·368	1·365	1·382
BC	1·436	1·434	1·420
CD	1·399	1·397	1·406
CE′	1·428	1·434	1·430
AG′	1·419	1·434	1·410





The comparison of the experimental results with various theoretical results, including several modifications of MO theory, is discussed in some detail in Cruickshank and Sparks' paper. The main point that emerged was that the simplest forms of the MO and VB theories both predict bond lengths for naphthalene and anthracene which correct to about 0·01 Å. These theoretical values are also shown in Table 1. The simple MO values given by Coulson *et al.*[18] have r.m.s. differences with experiment of 0·012 Å for naphthalene and 0·011 Å for anthracene, which are no greater than the errors to be anticipated from the known limitations of the method. Some half dozen corrections can be made to the simple MO theory, but none of these has a predominant effect. Inclusion of three of the more important corrections—self-consistency,

[17] A. Almenningen, O. Bastiansen and F. Dyvik, Private Communication.
[18] C. A. Coulson, R. Daudel and J. M. Robertsen, *Proc. Roy. Soc.* A **207**, 306 (1951).

variation of σ-bond energy with length, and configuration–interaction—gives somewhat better agreement (0·007 Å), though one fears that another correction might worsen it.

The earlier experimental results were in rather poor agreement with those predicted by the simple Pauling method, where the bond orders are given by the proportion of the Kekulé structures in which a particular bond is double. Its agreement with the latest results is excellent. In naphthalene AB has bond order $\frac{2}{3}$ and the other bonds $\frac{1}{3}$. In anthracene AB has order $\frac{3}{4}$, CD $\frac{1}{2}$ and the others $\frac{1}{4}$. These bond orders can be seen immediately to be in general agreement with the experimental results of Table 1, for in naphthalene AB is markedly the shortest bond, while in anthracene AB is again short, CD is intermediate and the other three bonds are long. The lengths shown in Table 1 in the column headed 'Pauling superposition' are those obtained from these π-bond orders p by the Pauling-type formula* for the length

$$r = 1{\cdot}477 - (1{\cdot}477 - 1{\cdot}337)\frac{1{\cdot}333p}{0{\cdot}333p + 1}$$

The constants in this formula are determined by the values of 1·337 Å for ethylene (bond order 1), 1·397 Å for benzene (order $\frac{1}{2}$) and 1·421 Å for graphite (order $\frac{1}{3}$). The formula extrapolates to a value of 1·477 Å for a single bond, which is seductively close to the estimates of about 1·48 Å obtained from molecules with unique classical structures, when both carbons are three-co-ordinated. The r.m.s. differences between the experimental results and those given by the Pauling method are only 0·006 Å for naphthalene and 0·007 Å for anthracene.

The change in fortune of the Pauling method offers a warning against undue trust in any but the most thorough experimental analyses. Though the earlier results were obtained by what were then advanced procedures, their accuracy was over-estimated. Similarly the estimates of accuracy of the present results may be falsified if further systematic errors are discovered—a sombre truism which applies to any experimental technique.

3. OTHER AROMATIC MOLECULES

Although many alternant aromatic hydrocarbons have been investigated by X-ray crystallography, very few have been refined to a degree comparable with that for naphthalene or anthracene, which now appears to be the minimum necessary for reliability. Such analyses require three-dimensional data with corrections for finite series, anisotropic vibrations and rotational oscillation effects. The results obtained by Burns and Iball[11] for chrysene (I) have e.s.d's of about 0·004 Å and are about as

I

accurate as those given above for anthracene. The r.m.s. discrepancies for the eleven independent CC bonds of chrysene are 0·016 Å for the simple MO theory and 0·015 Å

* The p in the numerator was inadvertently omitted in the printing of Cruickshank and Sparks' paper.[10]

for the Pauling method. The chief cause of these larger discrepancies is the value of 1·468 Å measured for the AB bond. This is 0·03–0·04 Å longer than the theoretical values and, as Burns and Iball point out, the reasonable explanation is that this bond is stretched as a consequence of the steric repulsion between the hydrogens attached to atoms C and I′. Other bonds will also be affected and the theories are thus not fully applicable to this slightly overcrowded molecule.

A similar overcrowding between hydrogen atoms seems to be the reason for the long 1·53 ± 0·01 Å *peri*-bonds connecting the naphthalenic residues in quaterrylene[12] (II). Of the 81 Kekulé structures for this molecule, none involve the *peri*-bonds as

II

double bonds; a length of 1·48 Å is therefore expected and it is reasonable to ascribe the increase to 1·53 Å as due to the overcrowding effect. Strictly this analysis by two-dimensional methods does not at all reach the specified standards of reliability, but as the 1·53 Å is an average for six independent *peri*-bonds, it is probably sufficiently accurate to be regarded as significantly longer than the expected 1·48 Å.

These difficulties of overcrowding can be avoided by replacement of CH by N at appropriate points of the rings. The remaining CC bonds can then be compared experimentally and theoretically. Such comparisons seem justified by the facts that the experimental results for acridine[19,20] and phenazine[21] show that their CC lengths are practically the same as the corresponding lengths in anthracene and because the MO bond orders for CC bonds in hydrocarbons and in the N-replaced molecules, with $\alpha_N = \alpha_C + 0{\cdot}5$, differ very little. Mason's experimental results[13,22] for 1·2:8·9-dibenzacridine in which there is no steric hindrance are therefore of potential interest. However the results published in 1960 as the conclusion of the work show an r.m.s. deviation between pairs of chemically equivalent bonds of 0·028 Å, which is almost three times as large as that of the interim results of 1957; one pair now differing by as much as 0·053 Å. Unfortunately the description of the refinement is very brief and no comment is offered on this difficulty: the trouble may be partly due to the fact that the data is only two-dimensional. Only the 1957 results were known to Cruickshank and Sparks, who found r.m.s. discrepancies between theory and experiment for the 12 CC bonds of 0·011 Å for the Pauling method and 0·008 Å for the MO method. In view of the poor internal consistency of the 1960 results it is not surprising that the two discrepancies now rise to 0·015 and 0·014 Å; the relative performance of the two theories at any rate remains similar.

4. COMPARISON OF MO AND PAULING METHODS

The good performance of both the simple MO and Pauling approaches to the determination of bond lengths in polynuclear aromatic hydrocarbons can be traced to

[19] D. C. Phillips, *Acta Cryst.* **9**, 237 (1956).
[20] D. C. Phillips, F. R. Ahmed and W. H. Barnes, *Acta Cryst.* **13**, 365 (1960).
[21] F. L. Hirshfeld and G. M. J. Schmidt, *J. Chem. Phys.* **26**, 963 (1957).
[22] R. Mason, *Nature, Lond.* **179**, 465 (1957).

a correlation of the two sorts of bond order. Fig. 1 plots MO bond orders against Pauling bond orders for fifteen representative molecules. To a first approximation there is a roughly linear relation in which as the Pauling π-order p varies from 0 to 1·0 the MO order m varies from 0·4 to 0·85. With appropriate choices for the order/length relations, this general correlation explains why both methods compare similarly with experiment. On more detailed examination striking results emerge if the bonds

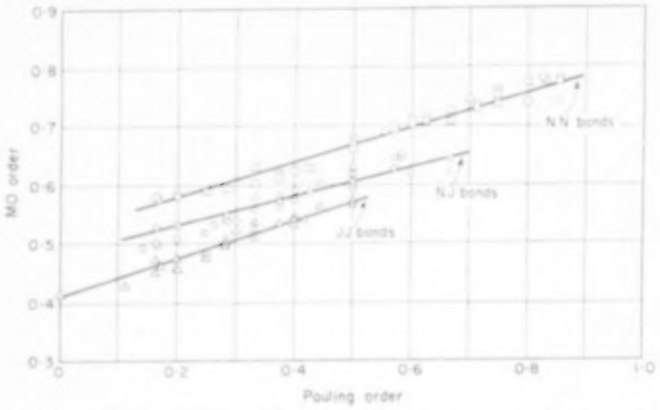


FIG. 1. The correlation of MO and Pauling bond orders. □, NN bonds; ○, NJ bonds; △, JJ bonds.
Vertical ordinate: MO bond order
Horizontal ordinate: Pauling bond order

are divided into three classes: NN, in which neither carbon atom is at the junction of two rings; NJ, with one atom at a ring junction; and JJ, with both atoms at junctions. The relations

$$m = 0{\cdot}52 + 0{\cdot}30p \text{ (for NN bonds)},$$
$$m = 0{\cdot}48 + 0{\cdot}25p \text{ (for NJ bonds)},$$
$$m = 0{\cdot}41 + 0{\cdot}33p \text{ (for JJ bonds)},$$

which are shown as straight lines in Fig. 1, then represent the correlation quite well.

For each theory Cruickshank and Sparks examined whether the experimental lengths showed different behaviour for the three classes, but the available results did not permit any unambiguous conclusions. The one evident conclusion from the experimental results was that the simple MO theory would do a little better if the theoretical order/length curve fell more steeply: this would accord with the wider spread of bond orders which more complete MO theories would show.

5. CONCLUDING REMARKS

The remarkably good behaviour of the Pauling or resonating-classical-structures method of determining bond lengths in aromatic molecules seems to fit in with the good performance of the unique-classical-structure method for non-aromatic hydrocarbons, granted that different standard lengths are used for the various coordination numbers. In view of the general defects of the simple MO method, typified by the excessive bond-order of the central bond in butadiene, it is perhaps surprising that it predicts bond lengths in aromatic molecules to within about 0·01 Å. Its good

VOL. 17 1962

performance seems due to the general correlation of its bond orders with the Pauling orders and to the use of a somewhat *S* shaped order/length curve (a more exaggerated *S* would mask the defects still further).

As implied previously, the only moderately accurate results which seem to be available for aromatic molecules free from steric hindrance are those for naphthalene and anthracene. Clearly more such molecules need to be studied; naphthacene, pyrene and coronene would be obvious early choices. The analogue of perylene formed by joining two isoquinoline units centrosymmetrically would also be worth investigation as it also would be free from steric hindrance. The length of its *peri*-bond would be of great interest as it has a bond-order of zero in the Pauling method and of about 0·4 in the simple MO theory, which presumably reduces to about 0·2 in more complete treatments. This length will thus be relevant to the discussion of the long bonds in butadiene, cyclo-octatetraene, diphenyl and 2·2′-dipyridyl, where the present evidence seems unfavourable even to the up-to-date MO theories.

In connexion with future X-ray investigations, it may be remarked that improvements in experimental techniques should make it possible[23] to determine bond lengths with e.s.d's of about one-third the best values mentioned above and reduced to, say, 0·0013 Å. Such accuracies should be possible in low temperature studies on the automatic counter diffractometers now starting to come into use, which are designed to measure thousands of reflexions quickly and accurately. Results of this precision will provide stringent tests for valence theories (and will cause the crystallographers the same kind of troubles over anharmonicity, etc., as are now experienced by spectroscopists and electron-diffractionists).

A final point can be introduced by way of Trotter's recent X-ray structure determination[24] of *p*-benzoquinone (III), in which the various desirable corrections were made. The measured bond lengths are C—O 1·222 ± 8 Å, C—C 1·477 ± 6 Å, C=C

III

1·322 ± 8 Å. These are close to the values expected in the classical–structure-method for bonds in these environments. Within experimental error, the value of 1·322 Å is not significantly different from a value of 1·337 Å in ethylene. However recalling that the C—C single bond in the paraffins[25,26] is of the order of 0·01 Å shorter than the C—C single bond in diamond, these two double bonds are not to be expected to have exactly the same length. This draws attention to the fact that the three reference points used to derive the order/length relation for the Pauling method were for ethylene, benzene and graphite, where each carbon has respectively two, one and no hydrogens as neighbours. In the rings of aromatic molecules no carbon is ever joined as in ethylene to two hydrogens, so that as a start to a more consistent approach it would be most valuable to have a modern redetermination of the C=C length in tetramethylethylene.[27]

[23] D. W. J. Cruickshank, *Acta Cryst.* **13**, 774 (1960).
[24] J. Trotter, *Acta Cryst.* **13**, 86 (1960).
[25] R. A. Bonham, L. S. Bartell and D. A. Kohl, *J. Amer. Chem. Soc.* **31**, 4765 (1959).
[26] D. R. Lide, *J. Chem. Phys.* **33**, 1514 (1960).
[27] L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.* **59**, 1223 (1937).

Tetrahedron, 1962, Vol. 17, pp. 163 to 169. Pergamon Press, Ltd. Printed in Northern Ireland

AN INVESTIGATION OF THE STRUCTURE OF BUTADIENE BY HIGH RESOLUTION INFRA-RED AND RAMAN SPECTROSCOPY

D. J. MARAIS,* N. SHEPPARD and B. P. STOICHEFF
University Chemical Laboratory, Lensfield Road, Cambridge
Division of Pure Physics, National Research Council, Ottawa

VOL. 17 1962

(*Received* 9 *January* 1961)

Abstract—The rotational Raman spectra of butadiene and butadiene-d_6 are found to consist of discrete lines having small ($\approx 0{\cdot}4\ cm^{-1}$) yet almost constant spacings, as would be expected for symmetric or nearly symmetric top molecules. An infra-red absorption band (Type C) of butadiene at 908 cm^{-1} is observed to have a spacing of about 2·5 cm^{-1}. Both the Raman and infra-red spectra provide evidence for the *trans* structure of the butadiene molecule. From the rotational constants A'' and $\tilde{B}''$ the following structural parameters were obtained: $\angle(C{=}C{-}C) = 122{\cdot}9 \pm 0{\cdot}5°$ and $r(C{-}C) = 1{\cdot}47_6 \pm 0{\cdot}010$ Å (somewhat shorter than recently determined from electron-diffraction experiments).

A. INTRODUCTION

THE butadiene molecule has proven to be a very useful example in discussions of valence theory, particularly in the calculation of fractional bond orders and the prediction of bond lengths. Yet, because of experimental difficulties and because of the rather complex structure of the butadiene molecule there have been only a few attempts to determine experimentally its structural parameters.[1] The most complete structural determination published so far is that of Almenningen, Bastiansen and Traetteberg who used the electron-diffraction technique. According to them the molecule has the *planar trans* configuration with $r(C{=}C) = 1{\cdot}337 \pm 0{\cdot}005$ Å, $r(C{-}C) = 1{\cdot}483 \pm 0{\cdot}01$ Å, $r(C{-}H) = 1{\cdot}082 \pm 0{\cdot}01$ Å, $\angle C{=}C{-}C = 122{\cdot}4°$ and $\angle C{=}C{-}H = 119{\cdot}8°$.

The purpose of the present paper is to report on the results of a high resolution study of the infra-red and Raman spectra of butadiene and on the information about the molecular structure obtained from these spectra.

B. THE INFRA-RED ABSORPTION BAND OF BUTADIENE AT 908 cm^{-1}

Most hydrocarbons containing a vinyl group have a strong infra-red absorption band near 900 cm^{-1} which is due to the hydrogen out-of-plane wagging motion of the $C{-}CH_2$ group.[2] An analysis of the vibration–rotation structure of this band in butadiene was undertaken in order to provide information about the rotational constants of the molecule, and in particular to confirm that it has the *trans* configuration.

The infra-red spectrum was measured on a grating spectrometer described previously[3] which had been modified to improve the uniformity of the grating drive.

* Present address: Merensky Institute for Physics, University of Stellenbosch, Stellenbosch, South Africa.

[1] V. Schomaker and L. Pauling, *J. Amer. Chem. Soc.* **61**, 1769 (1939); A. Almenningen, O. Bastiansen and M. Traetteberg, *Acta Chem. Scand.* **12**, 1221 (1958).
[2] N. Sheppard and D. M. Simpson, *Quart. Rev.* **6**, 1 (1952).
[3] R. N. Dixon, *Spectrochim. Acta* **9**, 59 (1957).

A Merton-type replica grating of 2500 lines per inch was used close to the first-order blaze at 10 μ. The detector was a Hilger-Schwarz thermocouple used with optical and D.C. amplification.

The absorption band is illustrated in Fig. 1. It is a Type C band, that is a perpendicular band in the limiting case of a symmetric top. Only the K structure was

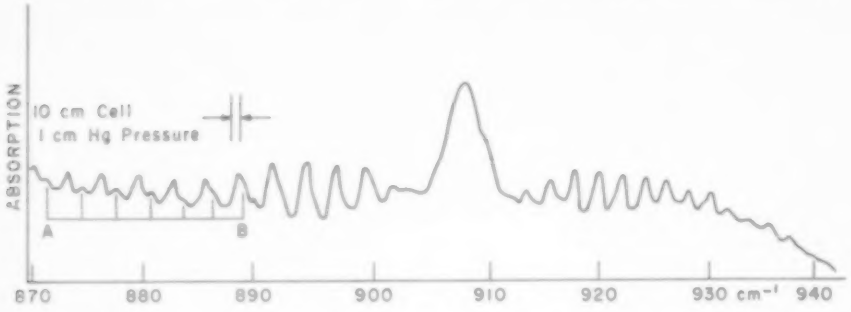


FIG. 1. The infrared absorption band of 1,3-butadiene centered near 908 cm^{-1} (Slit width = 0·8 cm^{-1})

TABLE 1. Absorption maxima for the CH_2 "wagging mode" of 1,3-butadiene

K	${}^{R}Q_K$ (cm^{-1})	${}^{P}Q_K$ (cm^{-1})	${}^{R}Q_K - {}^{P}Q_K$ (cm^{-1})	${}^{R}Q_K + {}^{P}Q_K$ (cm^{-1})
0	—	—	—	—
1	—	—	—	—
2	913·60			
3	915·65	901·80	13·85	1817·45
4	917·70	899·38	18·32	1817·08
5	919·80	896·80	23·00	1816·60
6	921·90	894·00	27·90	1815·90
7	923·93	891·18	32·75	1815·11
8	925·90	888·25	37·65	1814·15
9	927·80	885·40	42·40	1813·20
10	929·70	882·50	47·20	1812·20
11	931·60	879·50	52·10	1811·10
12	933·30	876·40	56·90	1809·70
13	935·00	873·30	61·70	1808·30
14	936·80	870·13	66·67	1806·93
15	938·35	—	—	—

resolved and the measured line positions are listed in Table 1. The combination differences ${}^{R}Q_K - {}^{P}Q_K$ and sums ${}^{R}Q_K + {}^{P}Q_K$ were plotted respectively against K and K^2 (Fig. 2) and from these the following band constants were obtained:

$$(A' - \tilde{B}') - (A'' - \tilde{B}'') = -0{\cdot}0287 \pm 0{\cdot}0008 \text{ cm}^{-1}$$

$$(A' - \tilde{B}') = 1{\cdot}20 \pm 0{\cdot}01 \text{ cm}^{-1}$$

$$(A'' - \tilde{B}'') = 1{\cdot}229 \pm 0{\cdot}01 \text{ cm}^{-1}$$

$$\nu_0 + (A' - \tilde{B}') = 908{\cdot}96 \text{ cm}^{-1}$$

The Q 'lines' can thus be represented by the formula $\nu = 908{\cdot}96 \pm 2{\cdot}40\,K - 0{\cdot}029\,K^2$, and the band origin ν_0 is at 907·76 cm^{-1}. A second set of lines, shown in Fig. 1 between A and B, has the same spacing as the main series and is probably caused by a 'hot' band.

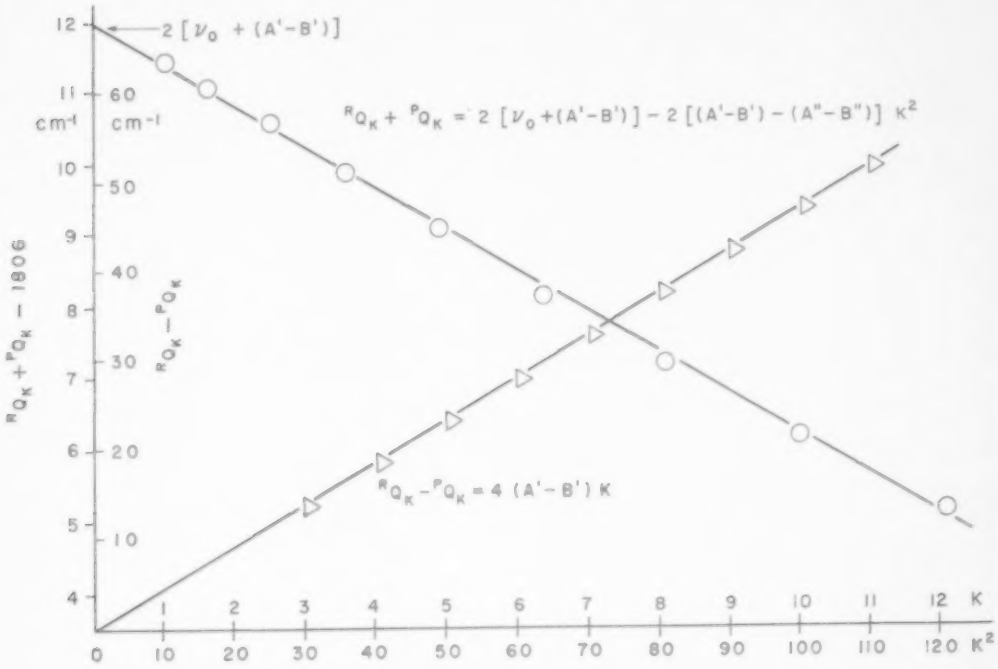


FIG. 2. Graphs of the relations ${}^RQ_K - {}^PQ_K$ vs. K and ${}^RQ_K + {}^PQ_K$ vs. K^2 for the 908 cm^{-1} band.

C. THE ROTATIONAL RAMAN SPECTRUM OF BUTADIENE

The pure rotational Raman spectrum of butadiene vapour at 15 cm Hg pressure was excited by the Hg 4358 line and photographed with a 21 ft grating spectrograph.[4] A rather simple line spectrum was observed as shown in Fig. 3. A similar spectrum, but with a narrower line spacing, was observed with butadiene-d_6. These spectra resemble the rotational spectra of symmetric or nearly symmetric tops. For nearly symmetric top molecules K remains a good quantum number and the selction rules for rotational transitions of symmetric tops in the Raman effect (namely $\Delta K = 0$; $\Delta J = 1,2$) still hold approximately. In the butadiene spectra only the S branch lines ($\Delta K = 0$; $\Delta J = 2$) were observed. Their frequencies are listed in Table 2.

The analyses of the spectra were carried out in the usual way making use of the symmetric top equation for the frequencies of the S lines

$$\Delta\nu = 4B''(J + 3/2) - 8D_J''(J + 3/2)^3$$

but with B″ replaced by $\bar{B}'' = \frac{1}{2}(B'' + C'')$. Graphs of $\Delta\nu/(J + 3/2)$ vs. $(J + 3/2)^2$

[4] B. P. Stoicheff, *Advances in Spectroscopy* (Edited by H. W. Thompson) Vol. I, p. 91. Interscience, New York (1959); *Canad. J. Phys.* **32**, 330 (1954).

Table 2. Frequency shifts of the rotational Raman lines of butadiene and 1,3-butadiene-d_6

J	$(\Delta\nu)$ cm^{-1}	
	$H_2C{-}CH{-}CH{-}CH_2$	$D_2C{-}CD{-}CD{-}CD_2$
17	10·470	
18	11·033	
19	11·595	
20	12·188	
21	12·718	
22	13·283	
23	13·826	
24	14·422	
25	14·989	
26	15·536	
27	16·111	13·179
28	16·658	13·653
29	17·206	14·105
30	17·776	14·548
31	18·304	15·008
32	18·803	15·468
33	19·433	15·929
34	19·997	16·404
35	20·569	16·840
36	21·187	17·306
37	21·737	17·775
38	22·320	18·256
39	22·882	18·726
40	23·444	—
41	24·009	19·671
42	24·563	20·125
43	25·130	20·539
44	25·690	20·993
45	26·256	21·470
46	26·819	21·932
47	27·368	22·375
48	27·935	22·824
49	28·488	23·293
50	28·914	23·732
51	29·590	—
52	30·188	—
53	30·774	25·235
54	31·338	25·686
55	31·929	26·142
56	32·485	26·578
57	33·060	27·009
58	33·639	27·456
59	34·182	27·910
60	34·730	
61	35·283	
62	35·849	

VOL.
17
1962

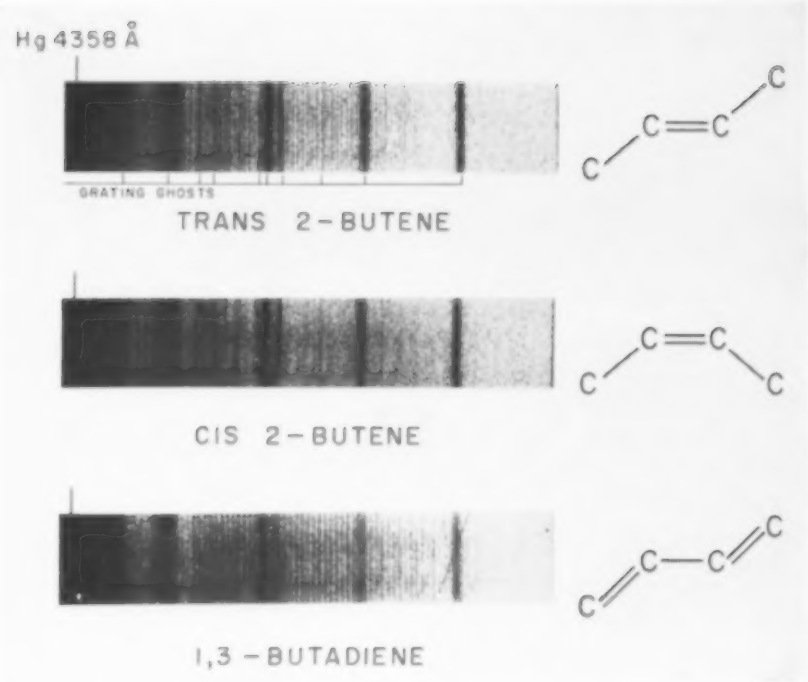


FIG. 3. The pure rotational Raman spectra of 1,3-butadiene, *trans* 2-butene, and *cis* 2-butene.

gave the values $\tilde{B}'' = 0{\cdot}1413 \pm 0{\cdot}0002\ cm^{-1}$ and $0{\cdot}1155 \pm 0{\cdot}0002\ cm^{-1}$ for C_4H_6 and C_4D_6 respectively (and $D_J'' \approx 1 \times 10^{-8}\ cm^{-1}$ for both). When combined with the value of $(A'' - \tilde{B}'')$ obtained from the infra-red band, this $\tilde{B}''$ value leads to $A'' = 1{\cdot}370 \pm 0{\cdot}011\ cm^{-1}$.

D. THE STRUCTURE OF BUTADIENE

The present spectroscopic results confirm the *trans* configuration of the butadiene molecule. A discrete rotational Raman spectrum would only be expected for the *trans* form since it deviates only slightly from a symmetric top whereas the *cis* form has a much larger deviation. For the latter, one would expect a complicated spectrum which would probably not be resolved under the conditions of the present experiment. The correctness of the above argument is supported by the rotational spectra of the *trans* and *cis* butene-2 molecules[4] included in Fig. 3: only the spectrum of the *trans* form has a discrete structure. Moreover, for butadiene the observed spacing of about $2{\cdot}5\ cm^{-1}$ in the infra-red band can be explained only by the *trans* form: for the *cis* form a spacing of about $1{\cdot}0\ cm^{-1}$ would be expected. Indeed the value of $A'' - \tilde{B}'' = 1{\cdot}229\ cm^{-1}$ observed here agrees quite well with that calculated from the structural parameters of butadiene given by Almenningen *et al.*[1], namely $A'' - \tilde{B}'' = 1{\cdot}213\ cm^{-1}$.

The spectroscopic results are not sufficient to determine the complete structure of the molecule, nor do they alone give definite proof for the planarity of butadiene. Nevertheless, if values of the CH_2 and CH parameters are assumed, it is possible to obtain reasonably accurate values of the parameters of the C=C—C = C group from the spectroscopic data. This method was adopted in the present calculations.

The following assumptions were made:

(1) butadiene is planar, that is, $I_C = I_B + I_A$

(2) all CH bonds have $r = 1{\cdot}085$ Å

(3) $\angle HCH = 120°$, $\angle CCH = 120°$.

It was then possible to calculate values of r(C—C) and I_A as functions of $\angle$(C=C—C) for various values of r(C=C) from the observed value of $\tilde{B}''$. These results are shown in graphical form in Figs. 4 and 5. (The observed value of $\tilde{B}''$ for butadiene-d_6 confirms these results but unfortunately does not lead to additional information.) The observed value of $I_A = (20{\cdot}43 \pm 0{\cdot}17) \times 10^{-40}\ g\ cm^2$ then leads to the relation (Fig. 5).

$$\angle(C{=}C{-}C) \pm 0{\cdot}5° = 149{\cdot}65 - 20\, r(C{-}C)$$

The relation between r(C—C) and $\angle$(C=C—C) shown in Fig. 4 expressed in equation form is

$$r(C{-}C) = 5{\cdot}716 - 1{\cdot}70\, r(C{=}C) - 0{\cdot}016\, \angle(C{=}C{-}C):$$

When the above relation for $\angle$(C=C—C) is substituted it reduces to

$$r(C{-}C) \pm 0{\cdot}008\ Å = 3{\cdot}3216 - 1{\cdot}380\, r(C{=}C)$$

This relation is represented by the broken lines in Fig. 4.

According to Almenningen *et al.*[1], the most accurately determined parameter of butadiene is the C=C bond length, $r(C{=}C) = 1{\cdot}337 \pm 0{\cdot}005$ Å. It is in good

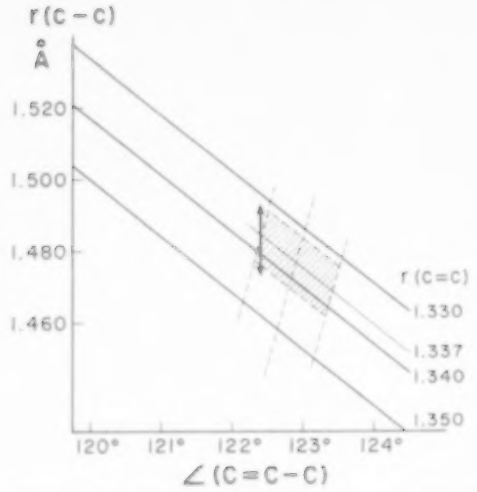


FIG. 4. Graph of r(C—C) vs. $\angle$(C—C—C) for various values of r(C—C) consistent with the observed value of $\bar{B}^{-}$. The hatched area represents the values of r(C—C) consistent with the observed value of I_A and r(C=C) = 1·337 ± 0·005 A. The vertical arrow represents the value of r(C—C) determined by electron-diffraction experiments.

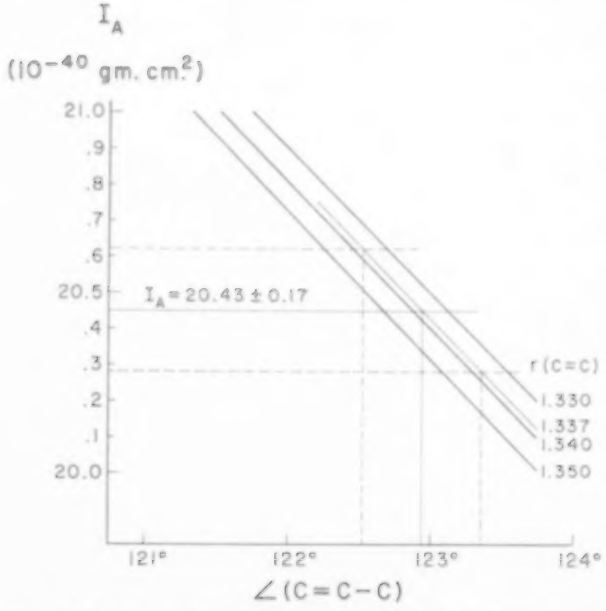


FIG. 5. Graph of I_A vs. $\angle$(C—C—C) for various values of r(C—C) consistent with the observed value of $\bar{B}^{-}$.

agreement with recent values of the C=C bond length in ethylene, namely 1·334 Å[5], 1·337 Å[6] and 1·339 Å[7]. If this value of r(C=C) = 1·337 Å is now taken over, the spectroscopic results give the related values of r(C—C) and ∠(C=C—C) represented by the hatched area of Fig. 4:

$$r(\text{C—C}) = 1{\cdot}476 \pm 0{\cdot}010 \text{ Å}$$
$$\angle(\text{C=C—C}) = 122{\cdot}9 \pm 0{\cdot}5^\circ$$

For purposes of comparison the values obtained by electron diffraction are indicated by the vertical arrowhead in Fig. 4. It may be mentioned that the electron-diffraction analysis indicates an unsymmetrical error distribution for r(C—C), making an error of +0·01 Å less probable than an error of −0·01 Å.

In conclusion, the spectroscopic data are in agreement with the structural parameters determined by electron diffraction within the quoted limits, although the spectroscopic data slightly favour a C—C bond length shorter by about 0·01 Å and a C=C—C angle larger by about 0·5° than the electron-diffraction values. Even so, this shorter value for the C—C bond length in butadiene still gives an appreciably higher value than would be expected (~1.460 Å) from the observed linear relation of the variation of C—C bond lengths with the total number of atoms adjacent to the C—C bond.[8]

Acknowledgements—We are grateful to Dr. L. A. Sayce of the National Physical Laboratory, Teddington, England, for the replica grating, to the Hydrocarbon Group of the Institute of Petroleum, England, for financial assistance, and to Dr. L. C. Leitch, of the National Research Council, Ottawa, Canada, for preparing the sample of butadiene-d_6.

[5] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* **27**, 1414 (1957).
[6] H. C. Allen and E. K. Plyler, *J. Amer. Chem. Soc.* **80**, 2673 (1958).
[7] J. M. Dowling and B. P. Stoicheff, *Canad. J. Phys.* **37**, 703 (1959).
[8] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* **30**, 777 (1959).

Tetrahedron, 1962, Vol. 17, pp. 171 to 175. Pergamon Press, Ltd. Printed in Northern Ireland

VOL. 17 1962

ELECTRONIC WAVE FUNCTION OF METHANE AND C—H BOND ORBITAL

LUIGI OLEARI*
Mathematical Institute, Oxford

(*Received* 25 *January* 1961)

Abstract—Using the delocalized bond orbital method, obtained as a linear combination of the sp^3 hybrid orbitals on the carbon and 1*s* orbitals on the hydrogens, we have calculated the energy of methane at the distances 0·9, 1·1 and 1·3 Å as a function of the orbital exponents. A discussion is given of the results in relation to the method of using a monocentric wave function on the carbon.

The energy at 1·1 Å is −40·122 a.u. and is in a rather good agreement with the results obtained by Mills and recently by Saturno and Parr.

The error with respect to the experimental value (0·4 a.u.) is of the order of the correlation energy.

INTRODUCTION

ALTHOUGH the bond between carbon and hydrogen is quite important in chemistry, nevertheless we know very little about it. The reason that the bond is rather peculiar is the small size of the hydrogen atom and the short length of the bond. If we look, for instance, at the centre of the charge-cloud of the sp^3 hybrid orbital of the carbon alone, we find that it is rather close to the position of the proton in the C—H bond. Of course in this situation the overlap between such a hybrid and the atomic orbital of the hydrogen is big and the hybrid itself is already a good approximation to the bond orbital.

The purpose of the present work is to study how well the usual approximation of the L.C.A.O. method applies to this kind of bond where one of the orbitals has the greatest role and to see what is the improvement compared with one of the other methods sometimes used to describe it, in which we use only monocentric orbitals on the carbon.[1–3]

CALCULATION

In almost all previous work on methane the delocalized molecular orbital method has been used with the four valence-shell atomic orbitals of carbon and the four 1*s* orbitals of the hydrogens as basis.[4,5]

In this case the chemical picture of a C—H bond loses some of its meaning.

Therefore, with the specific purpose of retaining the chemical significance of a bond, we introduce four localized molecular orbital bond orbitals ϕ_1, ϕ_2, ϕ_3, ϕ_4, one for

* Present address: Istituto di Chimica Generale, University of Padua, Padua, Italy.

[1] R. A. Buckingham, H. S. W. Massey and S. R. Tibbs, *Proc. Roy. Soc.* A **178**, 119 (1941).
C. Carter, *Proc. Roy. Soc.* A **235**, 321 (1956).
M. J. Bernal, *Proc. Phys. Soc.* A **66**, 514 (1953).
[2] I. Mills, *Mol. Phys.* **1**, 99 (1958).
[3] A. F. Saturno and R. G. Parr, *J. Chem. Phys.* **33**, 22 (1960).
[4] C. A. Coulson, *Trans. Faraday Soc.* **33**, 388 (1937).
[5] R. K. Nesbet, *J. Chem. Phys.* **32**, 1114 (1960).

each C—H bond, and we write the molecular orbitals of methane as linear combinations of these bond orbitals, with the correct symmetry of the tetrahedral group:

$$\Phi_1 = \frac{1}{2(1+3S)^{1/2}}[\phi_1 + \phi_2 + \phi_3 + \phi_4]$$

$$\Phi_2 = \frac{1}{2(1-S)^{1/2}}[\phi_1 + \phi_2 - \phi_3 - \phi_4]$$

$$\Phi_3 = \frac{1}{2(1-S)^{1/2}}[\phi_1 - \phi_2 + \phi_3 - \phi_4]$$

$$\Phi_4 = \frac{1}{2(1-S)^{1/2}}[\phi_1 - \phi_2 - \phi_3 + \phi_4]$$

Φ_1 is non-degenerate and of symmetry A; Φ_2, Φ_3, Φ_4, are degenerate with symmetry T, and S is the bond orbital overlap $\int \phi_1 \phi_2 \, d\tau$. The total molecular wave function is:

$$\Psi = \mathscr{A}(1s_C)^2 \Phi_1^2 \Phi_2^2 \Phi_3^2 \Phi_4^2$$

where the symbol $\mathscr{A}$ denotes an antisymmetrical product. Now each normalised bond orbital ϕ is written as a linear combination of a sp^3 hybrid orbital of the carbon and the corresponding $1s$ atomic orbital of a hydrogen:

$$\phi = N(q_C + \lambda q_H)$$

The sp^3 hybrid orbitals of carbon are obtained from $2s$ and $2p$ Slater orbitals, in which the $2s$ function is orthogonalized to the $1s_C$ orbital. In this way all the molecular orbitals are orthogonal to each other, except for the non-orthogonality of the λq_H terms in Φ_1 with the $1s_C$ of carbon; but the latter effect is negligable because this overlap is very small. The energy E associated with the wave function Ψ is a function only of one parameter λ (besides the exponents of the atomic orbitals ζ_C and ζ_H) and must be minimized with respect to it.

The calculations have been done for three bond lengths (0·9, 1·1 and 1·3 Å) and for several values of the orbital exponents ζ_C and ζ_H in the following ranges:

ζ_C from 1 to 2 (The Slater isolated-atom value is 1·625)

ζ_H from 0 to 2 (the isolated-atom value is 1)

ζ_{2s} and ζ_{2p} have been taken to be equal.

For the exponent of the carbon orbital $1s_C$ we have taken the Slater value of 5·7.

The complete description of the energy surface as a function of ζ_C and ζ_H at R = 1.1 Å is given in Fig. 1. For the other bond lengths the situation is analogous.

The best bond orbital wave functions at the several distances are the following:

$R = 0{\cdot}9$ Å $\quad \phi = 0{\cdot}8682\,(q_C + 0{\cdot}3211\,q_H)$

$R = 1{\cdot}1$ Å $\quad \phi = 0{\cdot}8512\,(q_C + 0{\cdot}2876\,q_H)$

$R = 1{\cdot}3$ Å $\quad \phi = 0{\cdot}7664\,(q_C + 0{\cdot}4324\,q_H)$

The corresponding energies are reported in Table 1, while in Table 2 we give the best energies and exponents for monocentric bond orbitals (These are obtained by putting $\lambda = 0$ in Ψ). All the bicentric integrals and penetration three-centre integrals

have been evaluated exactly. The other polycentric integrals have been evaluated by the Mulliken approximation:

$$\varphi_a\varphi_b \simeq \tfrac{1}{2} S_{\varphi_a\varphi_b}[\varphi_a^2 + \varphi_b^2]$$

In this work φ_a and φ_b are either sp^3 hybrid orbitals of carbon atom or pure 1s atomic orbitals of hydrogen atoms.

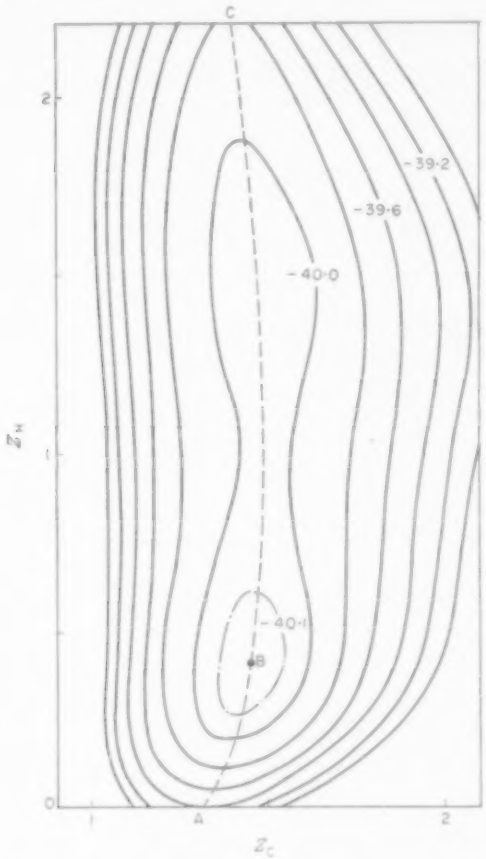


FIG. 1. The energy surface at $R = 1{\cdot}1$ Å as a function of ζ_C and ζ_H.

The equilibrium bond length was calculated using the following Morse expression:

$$E = E^0 + D(1 - e^{-a(r-r_e)})^2$$

where: $E^0 = -40{\cdot}1263$ a.u. $\quad a = 2{\cdot}0379$ Å^{-1}

$D = 0{\cdot}63$ a.u. $\quad r_e = 1{\cdot}0575$ Å

D is the dissociation energy.[2] The values for E^0, a and r_e are those which satisfy the calculated energies. The bond length calculated in this way is 1·058 Å.

DISCUSSION

The energy surface regarded as a function of ζ_C and ζ_H has the shape of a rather long and narrow basin in such a way that the energy is very sensitive to the variations of ζ_C and much less sensitive to ζ_H. The bottom of the basin is rather flat due to a certain compensation between the variations of ζ_H and λ in such a way that the energy does not change very rapidly. Of particular significance is the part of the surface close to $\zeta_H = 0{\cdot}2$ where the slope is great and shows that the improvement of the bond wave function due to the contribution of the hydrogen orbital is remarkable.

TABLE 1. ENERGIES AND ORBITAL EXPONENTS FOR THE BICENTRIC BOND ORBITALS MODEL OF METHANE

R (Å)	ζ_C	ζ_H	E (a.u.) total
0·9	1·59	0·3	−40·036
1·1	1·45	0·41	−40·122
1·3	1·57	0·78	−40·030

Drawing a line through the minimum points at several values of ζ_H we have the line A—B—C. The part B—C is rather straight with ζ_C constant in agreement with the fact that the greatest contribution to the bond orbital comes from the sp^3 hybrid and therefore is insensitive to the variations of the hydrogen orbitals. But the part A—B has a certain curvature in such a way that the best ζ_C for the monocentric orbitals is different from the best ζ_C in the bond orbitals, being always smaller than when bond orbitals are used.

TABLE 2. ENERGIES AND ORBITAL EXPONENTS FOR THE MONOCENTRIC BOND ORBITALS MODEL OF METHANE

R (Å)	ζ_C	E (a.u.) total
0·9	1·453	−39·274
1·0	1·375	−39·363
1·1	1·314	−39·366
1·2	1·264	−39·327
1·3	1·252	−39·280

This means that when we use monocentric sp^3 orbitals as bond orbitals, we are forced to compromise between the desire to place some charge around the H nucleus and also some other charge at the distance from the C nucleus which is appropriate to a normal carbon atom. This makes the monocentric orbitals more diffuse (smaller ζ_C) than for a normal carbon atom. However, as soon as we find an alternative way of placing charge close to the H nucleus, by introducing the term λq_H in the bond orbital ϕ, the sp^3 hybrids are free to resume their normal size, so that ζ_C increases. All this is very clear from Fig. 1.

It also shows us why, if we insist on using a monocentric expansion, we can only expect to get a good energy by introducing considerable configuration interaction.

The values of the energy are quite good and are slightly better than the recent values of Saturno and Parr[5] obtained with a very flexible monocentric wave function

TABLE 3. CALCULATED AND EXPERIMENTAL ENERGIES OF THE METHANE MOLECULE

	R (Å)	E (a.u.)
This work	1·1	−40·122
Mills*	1·058	−40·06
Saturno and Parr*	1·058	−39·804
Experimental	1·094(*)	−40·522(†)

* From Thomas and Welsh.[6]

† This value, according A. F. Saturno and R. G. Parr, assumes the heat of sublimation of carbon to be 169·58 kcal/mole.

(Table 3). However, the difference is small and we cannot say whether it is due to a better wave function or to the use of Mulliken's approximations in the evaluation of the polycentric integrals. The difference with the experimental value is small (0·4 a.u.) and is of the order of the correlation energy.

Acknowledgements—The author is particularly indebted to Prof. C. A. Coulson for many suggestions and discussions in the course of the work and for his kind hospitality at Oxford.

Grateful acknowledgement is made also to the National Council of Research (C.N.R. Italy) for the award of a fellowship.

[6] M. A. Thomas and H. L. Welsh, *Canad. J. Phys.* **38**, 1291 (1960).

VOL
17
190

Tetrahedron, 1962, Vol. 17, pp. 177 to 190. Pergamon Press, Ltd. Printed in Northern Ireland

ON INFERENCES OF BOND CHARACTER FROM BOND LENGTH; THE IMPORTANT ROLE OF NONBONDED INTERACTIONS[1]

L. S. BARTELL
Department of Chemistry, Iowa State University, Ames, Iowa

(*Received* 13 *January* 1961)

VOL. 17 1962

Abstract—Although experimental molecular structure is one of the oldest and most frequently applied diagnostic tools in studies of the nature of chemical bonds, it is concluded that its application to all but the grossest details of bonds such as carbon–carbon bonds remains entirely speculative. The concept of bond length is discussed to emphasize the need for careful consideration of ambiguities associated with the natural indeterminacy of atomic positions. A theoretical basis is given to the empirical Schomaker–Stevenson rule relating bond length to electronegativity. The divergent views of Pauling and Walsh on hybridization, ionic character, and bond strength are reconciled to some extent with the aid of a simple model. It is shown that structural effects commonly attributed to conjugation, hyperconjugation, hybridization, and partial ionic character can be rationalized to a remarkable extent in terms of nonbonded interactions. It is suggested that these factors are not fundamentally as distinct from each other as they are often assumed to be, and that much more serious attention should be given to the role of nonbonded interactions.

Of the numerous physical observables dependent in some way upon the nature of interatomic linkages, only a handful can be unambiguously ascribed to, and uniquely identified with, the various individual bonds. Such special observables have played important roles in our striving to understand chemical bonds. Of these the bond length, as measured by diffraction or spectroscopic methods, is one of the oldest and most popular, and the carbon–carbon bond has been one of the favorite subjects. That the detailed interpretation of results is still a matter of active controversy, even for such a simple linkage as the carbon–carbon bond, is a conclusive demonstration of the superficiality of our understanding of the chemical bond.

The pattern of response of C—C bond lengths to changes in environment is now reasonably well documented. In view of the firmness with which certain arbitrary interpretations of this response have become entrenched in much current writing, it seems worthwhile to consider alternative approaches to the problem.

The basis of interpretation of bond lengths is almost purely empirical. For covalent bonds, internuclear distances have been found to be reasonably well represented by sums of characteristic atomic radii.[2] Deviations from additivity are considered to reveal specific interactions which, in favorable cases, can be diagnosed. An unfortunate circumstance greatly impeding interpretations is that the data available for a given bond are far outweighed numerically by the large number of interactions of plausible physical significance that have been invented to account for the data. The factors most commonly acknowledged to influence bond lengths are:

(a) bond order, conjugation, hyperconjugation
(b) hybridization
(c) partial ionic character
(d) nonbonded interactions.

[1] This research was supported by a grant from the National Science Foundation.
[2] L. Pauling, *The Nature of the Chemical Bond* (3rd Ed.) Chap. 7. Cornell University Press, New York (1960).

To this list should really be added another factor which, while so self-evident as to appear trivial, has, unhappily, played a significant role in the study of bonds:

(e) experimental errors and differences in operational definitions of bond length. Although the above terms [except for (e)] are considered to represent distinct bond characteristics, precisely definable in principle even if they have not yet been in practice, a little reflection shows that they are more subtly interwoven than commonly recognized. Perhaps the best established of them is (a) in aromatic hydrocarbons as predicted by Pauling and co-workers.[3] Structural effects of the others listed have been less conclusively demonstrated and even (a) is speculative in nonaromatic molecules, with which we shall be concerned in the remainder of the paper.

Curiously, at least for bonds to carbon atoms, the most neglected of the factors, (d), gives promise of becoming one of the most important. It was recently pointed out[4] that if a plausible set of potential functions describing interactions between nonbonded atoms were adopted, carbon–carbon bond lengths in a variety of nonaromatic hydrocarbons could be closely computed without invoking hybridization, conjugation, or hyperconjugation. Since the arguments were also found to be applicable in large measure to bond energies and other thermochemical and kinetic effects[5] previously attributed to factors (a) and (b) above, it was suggested that nonbonded interactions might well be dominant factors in governing the changes in bonds accompanying changes in environment. The principal theme of this paper will be to point out some interrelationships between nonbonded interactions and the other factors listed which suggest that the concepts they represent are not as distinct as generally thought. In view of the preliminary nature of the new nonbonded model it seems best to present it in its most elementary form, keeping its oversimplifications obvious rather than masking them with physically reasonable corrections. Even in this form it leads to an unexpected range of correlation.

INTERPRETATIONAL UNCERTAINTIES IN BOND LENGTHS

Let us consider first factor (e) above, the problem of experimental errors and differences in definitions of bond length. The reason for concern is that the response of bond lengths to significant changes in environment is usually very small, and of a magnitude often not much greater than the above uncertainties. It has only been comparatively recently that experimental errors in the best diffraction studies have even approached a comfortable margin in this respect, say $\pm 0{\cdot}004$ Å or better, and that the full magnitude of interpretational uncertainties in spectroscopic studies has been recognized. In addition, virtually no effort has been made until recently to reduce bond lengths determined by different methods to comparable values.

When it is considered that the natural zero-point indeterminacy associated with atomic positions is of the order of 0·1 Å and that the probability distribution is asymmetric, it is readily apparent that the determination of interatomic distances will be sensitive to the method of averaging over bond vibrations. As simple schemes for treating the problem have not been fully worked out there are still interpretational uncertainties of the order of 10^{-2} Å in the case of C—C bonds. The C—H bond has

[3] L. Pauling, L. O. Brockway and J. Y. Beach, *J. Amer. Chem. Soc.* **57**, 2705 (1935); L. Pauling and L. O. Brockway, *Ibid.* **59**, 1223 (1937). For a recent review see D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.* A **258**, 270 (1960).

[4] L. S. Bartell, *J. Chem. Phys.* **32**, 827 (1960).

[5] L. S. Bartell, (to be published). A preliminary report is given in *Tetrahedron Letters* No. 6, 13 (1960).

VOL. 17 1962

received considerable attention, however, and it is instructive to study the results for the familiar series of hydrocarbons listed in Table 1. The parameters r_0, r_g, and r_e represent the spectroscopic average over the ground state,[6] the mean length, and the equilibrium length. The mean bond length, or center of gravity of the bond probability distribution, can be deduced from electron diffraction data for gas molecules.[7] X-ray crystal analyses, when corrected for thermal motions, give a parameter close to r_g.

TABLE 1. C—H BOND LENGTHS IN SEVERAL MOLECULES AS CHARACTERIZED BY VARIOUS DISTANCE PARAMETERS

Molecule	Hybridization[a]	Hybridization[b]	r_0[c]	r_g[d]	r_e[e]
HC≡CH	sp	sp^3	1·059[f]	(1·079)[g]	1·064[f]
$H_2C{=}CH_2$	sp^2	sp^3	1·086[h]	1·084[i]	(1·067)[j]
CH_4	sp^3	sp^3	1·094[k]	1·107[l]	(1·085)[j,l]
CH radical	p	sp^3 (?)	1·129	1·138	1·120[m]

[a] A. D. Walsh, reference 32; C. A. Coulson, reference 27.
[b] L. Pauling, reference 26 (CH radical not explicitly discussed).
[c] Spectroscopic average over ground state.
[d] Mean bond length, ground state.
[e] Equilibrium distance.
[f] B. D. Saksena, *J. Chem. Phys.* **20**, 95 (1952).
[g] Estimated from r_e.
[h] T. L. Allen and E. K. Plyler, *J. Amer. Chem. Soc.* **80**, 2673 (1958); Dowling and B. P. Stoicheff, *Canad. J. Phys.* **37**, 7034 (1959).
[i] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* **27**, 1414 (1957); *Ibid.* **31**, 400 (1959).
[j] Estimated from r_g.
[k] T. L. Allen and E. K. Plyler, *J. Chem. Phys.* **26**, 972 (1957).
[l] L. S. Bartell, K. Kuchitsu, and R. J. deNeui, *J. Chem. Phys.* **33**, 1254 (1960).
[m] G. Herzberg, *Infrared Spectra of Diatomic Molecules*. Van Nostrand, New York (1950).

For most of the entries in Table 1 standard errors are reported to be ±0·003 Å or less, but additional small uncertainties may arise. The important thing to observe is that the differences between r_0, r_g, and r_e, which are not always considered in comparing results for different molecules, are comparable to the differences from molecule to molecule. As a rule the C—C bond, with its smaller amplitude of vibration, will exhibit smaller differences between the various parameters than the C—H bond.

The value almost universally selected to represent the C—C single bond distance is the diamond X-ray value, 1·544 Å. Not only is this distance not an equilibrium distance as it is often taken to be (since zero-point motions undoubtedly expand the bond length in the lattice by the order of 0·01 Å), but it is appreciably higher than the C—C distances characteristic of paraffin hydrocarbons with r_g = 1·533 Å[9] and r_0 = 1·526 Å.[10] This is at least partly because of repulsions between nonbonded atoms.[11]

It is helpful to recognize that the decrease encountered in a given bond in going

[6] Actually r_0 as customarily used does not signify a unique physical quantity. It may or may not, depending on the case, be subject to errors arising from assumptions of equivalence of positions of atoms of different isotopic mass. See C. C. Costain, *J. Chem. Phys.* **29**, 864 (1958).
[7] Unfortunately, the commonest parameter reported for electron diffraction determinations is an "effective length", generally intermediate between r_g and r_e and often slightly larger than r_0. See L. S. Bartell, *J. Chem. Phys.* **23**, 1219 (1955).
[8] K. L. Lonsdale, *Phil. Trans. Roy. Soc.* A **420**, 1219 (1947).
[9] For a summary of electron diffraction and X-ray data for n-hydrocarbons see R. A. Bonham, L. S. Bartell, and D. A. Kohl, *J. Amer. Chem. Soc.* **81**, 4765 (1959).
[10] For propane and isobutane. D. R. Lide, *J. Chem. Phys.* **33**, 1514, 1519 (1960). Strictly, Lide's parameter is not r_0 but r_z, a related parameter presumed to lie somewhat closer to r_e.
[11] L. S. Bartell, *J. Amer. Chem. Soc.* **81**, 3497 (1959).

from r_g to r_e (i.e. from full to zero vibrational amplitudes) stems not only from the hypothetical settling of the bond to the bottom of its own anharmonic valence stretching potential well but also from the smaller nonbonded repulsions of neighboring atoms as they become quiescent. This latter factor leads us to predict that the mean C—C bond length in C_2H_6 should be a few thousandths of an angstrom longer than in C_2D_6 where the greater inertia of the D atoms restricts their vibrational amplitudes.

NONBONDED REPULSIONS

The underlying basis of the ideas in the remainder of the paper is that, contrary to prevalent opinion, the nonbonded repulsions between any two atoms bonded to a given carbon atom are enormous, and strongly influence structure and thermochemical properties. The factor that has obscured these repulsions is that they are balanced in tetrahedral compounds more closely than might have been expected. That is to say, interactions between the pairs H · · · H, C · · · C, Cl · · · Cl, H · · · C, and H · · · Cl, for example, are very similar in magnitude in substituted methanes. Notwithstanding, it has almost always been assumed that chlorine atoms are large and repel atoms strongly whereas hydrogens are small and quite negligible in comparison. Consequently it has been considered that bond angles, lengths, and energies in the series CH_nCl_{4-n} would show marked variations if nonbonded repulsions were large. The smallness of effects in this series was early interpreted[12] as indicating that atoms are greatly whittled down on the side of covalent bonds and hence exhibit small repulsions. Chemists have adhered to this belief.

The success of Pitzer and Catalano[13] in accounting for isomerization energies of paraffin hydrocarbons by a model invoking dispersion forces but altogether ignoring nonbonded repulsions (except for *gauche* configurations) is further evidence for the balance of the repulsions. The nonbonded interactions presently assumed, which have the dispersion forces of Pitzer and Catalano built into them, give a similar profile of interaction differences to account for isomerization energies.[14]

Confusing the picture have been the results of analyses of vibrational spectra. Urey–Bradley analyses offer, in principle, perhaps the most direct experimental resolution of molecular force fields into valence and central force components that has yet been devised. The confusion arose because repulsions were found by analyses to be strong,[15–17] of the magnitude required for the present model and entirely comparable with repulsions computed for intermolecular van der Waals forces at the same distance, except in the case of hydrogen atoms. For methane, H · · · H interactions seemed to be negligible.[16] Inasmuch as structural and thermochemical evidence did not permit the large imbalance implied by the spectroscopic analyses, chemists tended to ignore all repulsions of atoms bonded to a given C atom. Nevertheless, the range of information simply accounted for by the assumption that interactions, including H · · · H interactions, are large, seemed too broad for the assumption to be

[12] L. Pauling, *The Nature of the Chemical Bond* p. 193. Cornell University Press, Ithaca (1939).
[13] K. S. Pitzer and E. Catalano, *J. Amer. Chem. Soc.* **78**, 4844 (1956).
[14] The profile is not identical, however. It worked better for one reasonable model of molecular structure but not as well for the structural model of Pitzer and Catalano. Since our present emphasis is on the magnitude of, rather than the detailed differences between interactions, no parameter optimization has been attempted.
[15] H. C. Urey and C. A. Bradley, *Phys. Rev.* **38**, 1969 (1931).
[16] T. Shimanouchi, *J. Chem. Phys.* **17**, 245, 734, 848 (1949).
[17] J. W. Linnett and D. F. Heath, *Trans. Faraday Soc.*, **44**, 873, 878, 884 (1948); **45**, 264 (1949); *J. Chem. Phys.* **19**, 801 (1951).

VOL. 17 1962

altogether spurious. Accordingly, the preliminary paper[4] in this series proposed a strong hydrogen interaction potential and presented many of the following arguments.*

Since publication of this paper[4] the vibrational spectra of several simple hydrides, including methane, have been re-examined using considerably more detailed and precise spectroscopic data. Strong H · · · H nonbonded interactions were found[18] which agreed closely with the predicted[19] values. The most important features obscuring the interpretation previously were (i) the effects of anharmonicity which are far greater for light hydrogen atoms than for other atoms, and (ii) the neglect of stretch–stretch interactions. Consideration of these factors in an approximate treatment of neopentane has also improved the agreement between spectroscopic C · · · C interactions and those suggested in reference 4.

What makes it possible for the small hydrogen atom to compete in repulsive force with the larger carbon and chlorine atoms is that the larger atoms are further from the central atom, and the resulting increase in nonbonded distances closely compensates for the larger size.

Whereas the balance of repulsions masks their effect in tetrahedral molecules, the change in *number* of the repulsions upon going to trigonal and digonal molecules, leads to marked effects, as discussed in the following. The balance is also destroyed in strained cyclic molecules as cyclobutane, where, according to the present model, the relief of C · · · H repulsions counteracts significantly the increase in C · · · C repulsions as the C—C—C angle decreases from 109·5° to 90°. The magnitudes of the terms, which have been generally neglected in previous calculations of strain energies, are analysed in ref. 4. It is expected that similar considerations will prove to be important in conformational analysis. It is to be stressed, however, that the present interactions are entirely insufficient to explain the barriers to rotation around the C—C bond in ethane. They do yield, nevertheless, quite accurate values for the difference in energy between *trans* and *gauche* configurations of normal hydrocarbons.

Finally, it is fitting to mention that several theoretical papers[20,21] have appeared recently which seem to justify, at least partly, the present assumption that intramolecular interactions can be treated in much the same way as intermolecular van der Waals forces.

BOND ORDER

The principal environmental variation of bonds to be discussed in this paper is the variation in the number of adjacent bonded atoms.[22] A concise summary of behavior of carbon bond lengths is shown in Fig. 1. While the figure is schematic it quite

* After the present manuscript was completed, Professor E. B. Wilson, Jr., kindly brought to my attention a paper presenting similar ideas by J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *J. Amer. Chem. Soc.* **61**, 1868 (1939).

[18] L. S. Bartell and K. Kuchitsu (to be published). See also K. Kuchitsu and L. S. Bartell (submitted to *J. Chem. Phys.*). It is the second derivative of the nonbonded potential that is most accurately given by the data. Forces are less well established by direct analysis but can be estimated from $V''(r)$ with the aid of mild assumptions about $V(r)$.

[19] Reference 4. A recent estimate of interatomic H · · · H interaction energies very similar in magnitude at small r to the energies of reference 4 was published by J. T. Vanderslice and E. A. Mason, *J. Chem. Phys.* **33**, 492 (1960).

[20] R. McWeeny, *Proc. Roy. Soc.* A **253**, 242 (1959).

[21] O. Sinanoglu, *J. Chem. Phys.* **33**, 1212 (1960).

[22] The structural consequences of few other types of environmental changes have been followed sufficiently reliably for C—C bonds to warrant discussion here. But see J. D. Dunitz and V. Schomaker, *J. Chem. Phys.* **20**, 1703 (1952).

accurately characterizes a large body of data, as stressed by Bernstein, Costain, and Stoicheff.[23]

It has been customary to attribute a substantial part of the downward slope of the line representing single bonds to conjugative or hyperconjugative interactions. The point of view has been that delocalization of electrons from adjacent bonds into the bonding region of the single bond increases the effective bond order and shortens the C—C distance. Originally hyperconjugation was thought to be strongly effective only

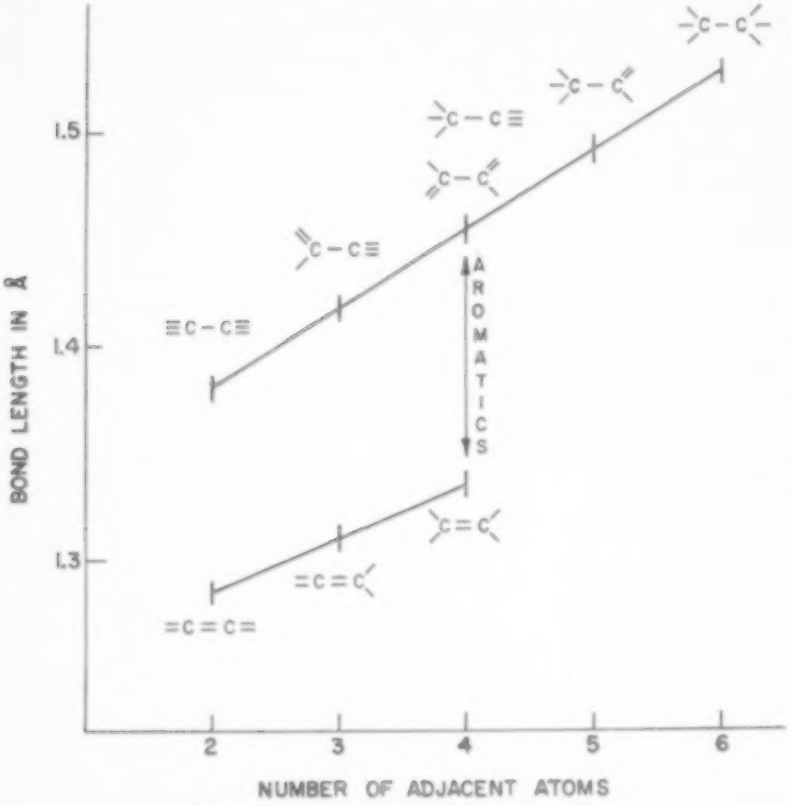


FIG. 1. Variation of bond length with environment.

when the adjacent single bonds were to hydrogen atoms, but substitution of the hydrogens by other atoms has been found to have surprisingly little effect on the C—C bond length.

Recently considerable doubt has been cast on the role of conjugation and hyperconjugation in the ground state of nonaromatic molecules on the basis of empirical evidence summarized by Dewar and Schmeising.[24] The character of the argument is not so much that conjugation and hyperconjugation are unreasonable as that, if proper account is taken of other factors, there remains little evidence for conjugative interactions in the molecules considered. It is interesting that the representation of

[23] H. J. Bernstein, *J. Phys. Chem.* **63**, 565 (1959); C. Costain and B. P. Stoicheff, *J. Chem. Phys.* **30**, 777 (1959).

[24] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959).

Bernstein[23] suggests a similar conclusion. Aromatic molecules, for which there is strong evidence[3] relating bond lengths to π bond orders, fall on a line terminated at Bernstein's pure single bond limit by the —C=C— and ≡C—C— bond lengths. Even before the idea of conjugation was seriously challenged it had often been observed that extrapolation of aromatic bond lengths to zero π bond order led to a value appreciably below that of the "normal" single bond.

A theoretical investigation of butadiene by Berry[25] has also lent weight to the idea that conjugation is of only minor importance in bond lengths. Moreover, Berry showed that there is no meaningful way, even granting that an adequate electronic wave function be known for a molecule, of exactly separating the contributions to bond stability of the electronic factors he examined. The reason for this is that components of the wave functions associated with the factors were not mutually or thogonal. It is perhaps along the lines of this argument that a theoretical test can be made of the present empirically justified suggestion that conjugation, hybridization, electronegativity and nonbonded interactions do not represent entirely distinct quantities. For the present, since pure theory as yet offers scant help, there is utility in continuing our empirical search for the simplest and most fruitful description of molecules.

To return to the theme of nonbonded interactions, it is to be noted that atomic repulsions across bonds increase in number as we proceed from left to right across Fig. 1. This is true both for single bonds and double bonds. Furthermore, if the nonbonded potential functions are known as a function of distance, repulsive forces can be evaluated and resolved along bond directions, and the influence on bond distance can be calculated from known force constants. It is interesting that the potential functions of ref. 4, constructed from considerations of intermolecular van der Waals forces, reproduce not only the directions but also the magnitudes of the slopes of the lines in Fig. 1. Since adjacent multiple bonds would be expected to introduce no appreciable π bond character into C—H bonds, it might be argued that a comparison of C—C and C—H bond shortenings would reveal the π character of C—C bonds. Pauling,[26] Coulson,[27] and others have indeed attributed the difference between C—C and the analogous but smaller C—H bond shortenings illustrated in Table 1 to π electron conjugation. It is found, however, that the nonbonded model also accounts for the smaller shift of the C—H bonds,[28] partly because of the larger force constants, and partly because of the geometry and magnitudes of repulsions. Similarly, the difference between C—Cl bonds in methyl and vinyl chlorides, which is larger than the analogous difference between C—C bonds, can be accounted for by the nonbonded model as well as by the conjugation model.[29] The present model would also predict

[25] R. S. Berry. *J. Chem. Phys.* **30**, 936 (1959).
[26] L. Pauling, *loc. cit.* (2), Sec. 5.
[27] C. A. Coulson, *Valence* Chap. VIII. Clarendon Press, Oxford (1952).
[28] Note, however, that the present nonbonded model, as applied using the potential functions of ref. 4, is not intended to treat bonds which are adjacent to unshared electrons, as the bond in the C—H radical. It has often been remarked that unshared electrons behave as bulkier groups than attached atoms, as suggested, for example, by bond angles and distances in NH_2 and the NH_2 radical (and the long bond in the C—H radical).
[29] The field gradient perpendicular to the bond observed at the chlorine nucleus in vinyl chloride has been interpreted in terms of a finite but small C—Cl double bond character. See J. H. Goldstein, *J. Chem. Phys.* **24**, 106 (1956). It seems possible that the different field asymmetries in vinyl chloride and methyl chloride may arise from polarization differences induced in the chlorine atoms by the different nonbonded environments.

VOL. 17 1962

shortenings in single bonds adjacent to three and four membered rings where increased nonbonded distances presumably relieve repulsions.

Another effect which has been regarded as strong evidence for hyperconjugation is a kinetic beta deuterium isotope effect discovered by Lewis[30] and Shiner[31] in solvolysis reactions. Here again nonbonded repulsions can be shown to provide an alternative explanation.[5] Hydrogen atoms, with characteristically larger amplitudes of vibration than deuteriums, behave as if they were bulkier and, accordingly, strive more vigorously to force off the leaving group and to make the carbon skeleton assume the trigonal configuration associated with the carbonium ion transition state. Numerical computations show the effect is entirely reasonable in magnitude, but the numerical values depend so strongly upon assumed bond angles and lengths (which at present are largely conjectural) that a definite conclusion cannot yet be made. The best estimate suggests that some hyperconjugative delocalization occurs but that this has the effect, in turn, of enhancing the nonbonded effect.[5] In any event, physical arguments for hyperconjugation in carbonium ion transition states seem much more convincing than for ground states of olefins.

As suggested above, even if conjugation were inescapable, considerations of nonbonded repulsions would inevitably arise. Valence bond structures written with π bonds across (nominally) single bonds imply, by the altered pairing scheme and charge distribution, a substantial reduction of certain nonbonded repulsions in the vicinity of the bond.

HYBRIDIZATION

By hybridization we shall mean to imply not only the geometry (tetrahedral, trigonal, digonal) but also *s*, *p*, etc. character of the sigma bonds. Walsh[32], especially, has stressed the number of properties that can be correlated in terms of hybridization and his ideas have gained widespread support. The original unavoidable oversimplifications have become deeply rooted with repeated usage and hybridization is now commonly regarded as a true physical property. In reality, of course, *s* character has always been used only as a parameter of correlation and never as an observable. There is no difficulty, given a simple valence bond or localized molecular orbital wave function, in assessing the hybridization. The difficulty is that there is as yet no unique way of defining hybridization in a many electron polyatomic wave function of sufficient complexity to treat rigorously such delicate things as bond angles. Granting this, no combination of experimental observables can be expected to establish hybridization. Nevertheless, the concept of hybridization is so attractive that we may confidently look forward to its ultimate clarification.

Two well-known alternative representations of hybridization of carbon orbitals in unsaturated molecules, the conventional σ–π description used for example by Walsh[32] and Coulson,[27] and Pauling's bent bond scheme[33] are listed for C—H bonds in Table 1. Neither scheme can yet be said to have been demonstrated clearly superior, and both are, at best, rough approximations.

The commonest diagnostic criterion used to infer hybridization in molecules is the angle between bonds. If a simple valence bond wave function is adopted, if it is

[30] E. S. Lewis and C. E. Boozer, *J. Amer. Chem. Soc.* **74**, 6306 (1952); *Ibid.* **76**, 791, 795, (1954).
[31] V. J. Shiner, Jr., *J. Amer. Chem. Soc.* **75**, 2925 (1953); *Ibid.* **76**, 1603 (1954).
[32] A. D. Walsh, *Trans. Faraday Soc.* **43**, 60 (1947).
[33] L. Pauling, *loc. cit.* (2), p. 137.

VOL. 17 1962

assumed that only *s* and *p* orbitals are involved, and if it is assumed that bonds are not bent, then it is an easy problem to compute bond angles as a function of hybridization.[34] None of the assumptions are clearly justified and much evidence has recently been cited regarding the failure of the last assumption.[4,35] Since the reasoning behind the assumption about unbent bonds is based on the principle of maximum orbital overlap, it is appropriate to point out an inconsistency. If Slater orbitals as tabulated by Mulliken *et al.* are used for ethylene,[36] and the H—C—H bond angle is increased or decreased symmetrically from the equilibrium angle, the sum of the overlaps of the bonding orbitals can be readily calculated. It is found to be about fivefold less costly in loss in overlap to *fix* the hybridization of the carbon orbitals at an optimum value and "bend" the C—H bonds than it is to *vary* the carbon hybridization to follow the angular displacements. Moreover, the known weakness of the bond bending restoring forces allows even modest nonbonded repulsions to alter bond angles by many degrees. These arguments reinforce the empirical observation of ref. 4 that bond angles seem closely correlated with "intramolecular van der Waals radii". They also strongly indicate that equilibrium bond angles are poor gauges of hybridization.

Dewar and Schmeising,[21] having presented impressive evidence against the importance of conjugation and hyperconjugation in nonaromatic molecules, chose to attribute the effects under discussion to hybridization changes,[37] following Walsh[32]. The authors pointed out that if the differences between tetrahedral and trigonal sigma bonds were taken explicitly into account, little thermochemical evidence for conjugation remained. The necessary differences in bond energy, $(E'_{CC} - E_{CC})$ and $(E'_{CH} - E_{CH})$ were determined empirically from experimental curves of bond energy versus bond length in conjunction with measured differences between trigonal and tetrahedral bond lengths. Again it may be remarked that direct use was not made of hybridization, but only of the geometry customarily associated with hybridization.

It is extremely interesting and probably significant that the nonbonded model leads only not to the same qualitative results as the model of Dewar and Schmeising, but in addition, permits a rough theoretical calculation of the slope, dE/dr, of the curve of bond energy versus bond length evaluated empirically by Dewar and Schmeising. Let us, naively, assume that bond energy is of the form

$$E = E_0 + \tfrac{1}{2}k(r - r_m)^2 + V_{nb} \tag{1}$$

where k is the force constant, r the bond distance, r_m a constant, and V_{nb} represents a variable environment of nonbonded repulsions across the bond between the atoms in the bond and atoms adjacent to the bond (of variable number). If we give V_{nb} the Lennard–Jones repulsive form, λr_{ij}^{-12}, it follows that

$$dE/dr \sim -kr_{ij}/12(\partial r_{ij}/\partial r), \tag{2}$$

independently of assumptions about the magnitude of λ. If the representative values $k \sim 4{\cdot}5 \times 10^5$ dynes/cm, $r_{ij} \sim 2{\cdot}5 \times 10^{-8}$ cm, and $(\partial r_{ij}/\partial r) \sim \sin(109{\cdot}5/2) \sim 0{\cdot}8$

[34] The converse problem of computing hybridization from an arbitrary set of bond angles may not always have a solution.

[35] D. F. Heath, J. W. Linnett, and P. J. Wheatley, *Trans. Faraday Soc.* **46,** 137 (1950). N. V. Cohan and C. A. Coulson, *Ibid.* **52,** 1163 (1956); L. Burnelle and C. A. Coulson, *Ibid.* **53,** 403 (1957). N. Muller and D. E. Pritchard, *J. Chem. Phys.* **31,** 1471 (1959). Casabella, Bray, and Barnes, *Ibid.* **30,** 1393 (1959).

[36] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.* **17,** 1248 (1949). The conventional σ-π double bond representation was assumed in the present computation and all bond lengths were fixed.

[37] Paper II by M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **11,** 96 (1960), introduces, however, the qualification that nonbonded interactions are to be considered absorbed into hybridization.

are substituted into equation (2), it is found that the magnitude of dE/dr is 170 kcal/mole per angstrom. Dewar and Schmeising, by solving simultaneous equations involving energies of formation of various hydrocarbons of known structure, found slopes at normal single bond distances of about 250[24] or 190[37] for C—C and 150[24] or 250[37] for C—H bonds, in the same units. Glockler[38] has reported analogous values of 140–190 and 140, respectively. The fact that the nonbonded model gives slopes agreeing with slopes determined with the use of C—C bonds of obviously variable bond order is of obscure significance.[39] The fact that it provides correct magnitudes for Dewar and Schmeising's model to work is provocative evidence that the nonbonded model may be substituted in part, or in total, for the "hybridization" model with little change in effective result.

IONIC CHARACTER AND ELECTRONEGATIVITY

Although there is general agreement that the strength and length of bonds is markedly influenced by ionic character, the direction of the effect is still a matter of dispute. Pauling[40] has advanced a scheme, rationalized on the basis of ionic-covalent resonance, in which ionic character enhances bond energies and decreases lengths. The scheme, in which the concept of electronegativity plays a central role, is so successful in a wide variety of correlations that it is unthinkable to disregard it. This, of course, does not mean that the physical basis of its rationalization is necessarily correct. On the other hand Walsh[32] has given quite reasonable arguments that increasing ionic character weakens and lengthens bonds, and has concluded that ionic-covalent resonance is not a significant factor. Several illuminating discussions of of the two points of view have appeared.[41] It seems worthwhile to present a few additional ideas which, in a simple way, cast a little more light on interrelations between the two points of view. They will also give some insight into the nature of carbon–carbon bonds despite the fact that such bonds are not usually discussed in terms of ionic character.

In the case of the C—H bonds listed in Table 1, the hydrogens become more acidic as the bond configurations progress from tetrahedral to digonal. Presumably a similar shift of charge occurs in the analogous series of C—C bonds when H is replaced by CH_3. According to Walsh[32] and Coulson[27], among others, a dominant factor in the above series of bonds is that the electronegativity operative in the direction of a bond varies as the hybridization varies, and increasing the *s* character of a carbon orbital decreases the orbital radius, increases the electronegativity, and shortens the bond. Alternatively, Pauling[26] suggests a fixed hybridization where, as the bonds adjacent to a given single bond are bent to form double bonds or triple bonds, the nonbonding charge is bent away from the given bond direction. This would be expected to decrease nuclear screening, increase electronegativity and shorten the single bond. The essential similarity between the concept of bond–bond repulsions and interactions between pairs of nonbonded atoms,[42] implies a close similarity between Pauling's model and the nonbonded model of this paper.

[38] G. Glockler, *J. Chem. Phys.* **21,** 1291 (1953); *J. Phys. Chem.* **61,** 31 (1957).
[39] A partial explanation is given in the next section.
[40] L. Pauling, *loc. cit.* (2), Chapter 3.
[41] See, for example, A. D. Walsh, *Ann. Rev. Phys. Chem.* Vol. 5, p. 163, (1954) and "A discussion of bond energies and bond lengths," *Proc. Roy. Soc.* A **207,** 1–133 (1951).
[42] See T. L. Allen, *J. Chem. Phys.* **31,** 1039 (1959); H. J. Bernstein, *J. Chem. Phys.* **19,** 140 (1951); *Ibid.* **20,** 263, 524, 1328 (1952).

The relationship between bond lengths and electronegativity was first critically examined by Schomaker and Stevenson[43] who formulated the empirical rule for pure single bonds

$$r_{AB} = r_A + r_B - \beta\,|x_A - x_B|\,, \tag{3}$$

where r_A and r_B are "covalent radii", β is a constant equalling 0·09 Å and x_A and x_B are electronegativities. Pauling[40] has recently revised the rule by varying β in order to diminish discrepancies discussed by Wells,[44] and has adjusted the value to 0·08 Å for bonds to carbon atoms. No theoretical justification of equation (3) seems to have been given, though frequent criticism has been expressed that it holds only roughly and fails appreciably in many individual cases. Its failures can hardly be surprising in view of the abundance of effects thought to influence bonds, and in view of the fact that a satisfactory explanation of why bond lengths should be additive in the first place, has never been found. Nevertheless the trend successfully reproduced by the rule warrants further attention.

VOL. 17 1962

A clue to the possible significance of the Schomaker–Stevenson rule is provided by the ideas which led to Pauling's original definition of electronegativity. It is to be emphasized that the empirical definition in terms of deviations, Δ, from additivities of bond energies (or deviations, Δ', from the geometric mean of bond energies) seems almost accidentally to have captured considerable truth in terms of what we normally understand by electronegativity. Let us proceed with Pauling's original argument that a bond A—B, formed in the absence of an electronegativity difference has a bond energy, D_{AB}, given by the mean of D_{AA} and D_{BB}. Similarly, we assume r_{AB} is the mean of r_{AA} and r_{BB}, or sum of r_A and r_B. We then imagine that an "electronegativity difference" be turned on which results in an additional potential, $\lambda V'(r)$. For sake of argument we shall represent the bond potential energy by the sum of a Morse curve and $\lambda V'(r)$ as follows,

$$V(r) = D_0\{e^{-2a\Delta r} - 2e^{-a\Delta r}\} + \lambda V'(r) \tag{4}$$

where $\Delta r = r - (r_A + r_B)$ and D_0 is the mean of D_{AA} and D_{BB}. For any assumed form of $V'(r)$ it is possible to eliminate λ and establish a functional relationship between total depth, $D_{AB} = D_0 + \Delta$, of $V(r)$ and the position, $r_{AB} = r_A + r_B - \Delta r_{AB}$, of its minimum. Finally, the shift in bond length, Δr_{AB}, is related to electronegativity by Pauling's definitions

$$|x_A - x_B| = (\Delta/23)^{\frac{1}{2}} \tag{5}$$

or

$$|x_A - x_B| = (\Delta'/30)^{\frac{1}{2}}, \tag{6}$$

where energy is expressed in kcal/mole. The result of this elementary approach is shown in Fig. 2 for several simple forms of V', and compared with the Schomaker–Stevenson curve.

Fluorine, as it is the most electronegative element by far, is the element for which the need for corrections is most conspicuous. Since the unusually low bond energy and associated long bond length of elemental fluorine have been explained in terms of exceptionally large nonbonded repulsions on the one hand,[45] or low dispersion forces

[43] V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.* **63**, 37 (1941).
[44] A. F. Wells, *J. Chem. Soc.* 55 (1949).
[45] See, for example, J. K. Wilmshurst, *J. Chem. Phys.* **33**, 813 (1960). K. S. Pitzer, *Quantum Chemistry* p. 166, Prentice-Hall, New York (1953), discusses the analogous weakness of the O—O single bond on much the same basis.

on the other,[46] and since these interactions might be disproportionately relieved or augmented on bonding with other atoms, it seemed not unreasonable to try forms $e^{-r/\rho}$ and r^{-6} for V'. An alternative explanation of the electronegativity effect on the basis of nuclear repulsions[41] suggested as a lower limit of rate of variation the form r^{-1}. The effect of enhanced covalent binding was examined by using as V' the attractive part, of form $-e^{-ar}$, of the Morse curve. The effect of nonbonded neighbors as given in equation (1) was also calculated. For the purpose of application to bonds similar

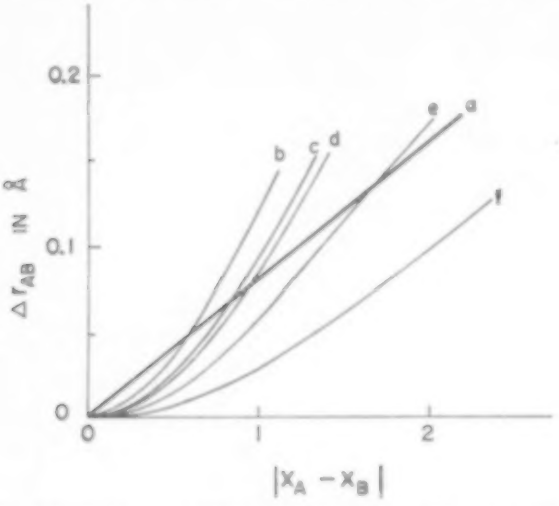


FIG. 2. Bond shortening as a function of electronegativity difference according to the Schomaker–Stevenson rule (a), and models where V' represents: (b) nonbonded atoms (equation 1), (c) $\exp(-r/\rho)$, (d) r^{-6}, (e) Morse bonding, (f) r^{-1}.

to C—C bonds, the values chosen for D_0, a, and ρ were 81 kcal/mole, 2 Å^{-1}, and 0·32Å, respectively. The general magnitude of the results was not sensitive to these parameters.

The most remarkable result is that the various forms assumed for V', *with no freely adjustable parameters*, lead to rather similar curves, and show a striking area of agreement with the empirical Schomaker–Stevenson rule[47]. For electronegativity differences that are not too large, except for $V' = r^{-1}$, the disagreement is of a magnitude comparable with experimental errors characteristic of the time of formulation of the rule. It seems reasonable to conclude, then, that the present arguments constitute a rough justification of the Schomaker–Stevenson rule[48]. Further, they remind us of how much more complex a property electronegativity is than a simple gauge of polarity.

We have now arrived at an approximate relation between bond length and electronegativity, and between bond length and shift from tetrahedral to trigonal bonds. This permits us to assess, or at least to speculate upon, the shift in electronegativity

[46] K. S. Pitzer, *J. Chem. Phys.* **23**, 1735 (1955).

[47] Schomaker and Stevenson always had reservations about the analytic form of their rule at zero electronegativity difference (c.f. their footnote 5). The present curves give a more appropriate slope in this region.

[48] Wilmshurst, ref. 45, also proposes an equation of the form of the Schomaker–Stevenson rule but concludes that increases in electronegativity difference tend to *increase* bond lengths. Allowances are made in the same equation for amount of *s* character, however, and the rather numerous assumptions introduced to establish *s* character markedly influence the apportionment between hybridization and electronegativity effects.

with the nonbonded relief or altered nuclear screening attending the shift from tetrahedral to trigonal bonds. For C—C bonds such a shift (in conventional but possibly misleading language, from "sp^3–sp^3 bonds" to "sp^2–sp^3 bonds") results in a decrease in bond length of 0·03 Å.[4] According to the various curves of Fig. 2, this is associated with an electronegativity shift of 0·4 to 0·6. From Pauling's relationship between ionic character and electronegativity[40] we deduce an "ionic character" of about 0·06 which, for a bond 1·5 Å long implies a dipole moment of 0·4 D.[49] This may be compared with the experimental dipole moments of 0·35 D when CH_3 is attached to a vinyl group, and 0·37 D when it is attached to a phenyl group.[50] It is quite common to attribute these moments to hybridization or hyperconjugation. Other hydrocarbon moments in nonaromatic networks as, say, methyl acetylene, methylcyclopropane, and methylcyclobutane can be accounted for similarly.

VOL. 17 1962

The fact that the moment in chlorobenzene is smaller than that in methyl chloride is likewise understandable in terms of the greater "electronegativity" of the carbon in the unsaturated compound. This leads us, however, directly to the apparent inconsistency which was alluded to at the beginning of this section, and indicates that *group* electronegativities, as portrayed by our scheme, do not share the same range of simple correlations as atomic electronegativities. The C—Cl bond length is shorter and bond energy is greater in chlorobenzene or vinyl chloride than in methyl chloride, and by the amount required by our parametric relation involving electronegativity. Accordingly it is natural to consider the electronegativity difference between $H_2C{=}CH-$ and Cl as being *greater* than between H_3C and Cl on the basis of the relation between electronegativity and energy. But, as we also showed from the model, the "hybridization" of carbon is such as to *reduce* the electronegativity and polarity differences in the unsaturated halides. A similar inconsistency is encountered in comparing the fluroides of CF_3 and CH_3 or halides of $C(CH_3)_3$ and CH_3. Whether this is at all related, by analogy to the present model, to the notably small size of fluorine atoms or large size of carbons in comparison with their covalent radii is not certain. Presumably, completely analogous arguments are also applicable to the C=O bond as it exists in, say, acetone and ketene. It was carbon–oxygen bonds, especially, that led Walsh to his conclusions about ionic character weaking bonds.[51] In any event, the ambivalent

[49] The above argument is oversimplified to draw quick attention to the principal point. Obviously in toluene, for example, the para hydrogen has a demand made upon it that is similar to that made upon the methyl group, and if its response were the same, the model would give zero dipole moment. But the present model implies a smaller Δr_{CH} than Δr_{CC}, and accordingly a smaller energy, electronegativity, and polarity shift for the hydrogen. It is striking that the discrimination needed between $(E'_{CC} - E_{CC})$ and $(E'_{CH} - E_{CH})$ for the model of Dewar and Schmeising to work is also needed to yield the correct dipole moments. So again we see a familiar correlation of the hyperconjugation theory, involving the donor capacity of H and CH_3, arising naturally from the present model.

[50] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* p. 108. Cornell University Press, New York (1953).

[51] In applying our nonbonded model the important effects of substituting atoms of different intrinsic electronegativity must, unfortunately, be neglected. That is because such cases would involve differential steric effects and we claim at present to know at most the magnitudes of the interactions, not the detailed differences between them. In the limited scope of environmental variations left for us to explore we should choose to express Walsh's connection differently, stating that the environmental factors leading to bond strengthening also lead, in Walsh's bonds, to smaller polarity differences. If the bond from carbon were to an atom, Y, of *lower* intrinsic electronegativity than carbon, bond strengthening in our model would be associated with *increased* bond polarity. The hybridization model of Walsh would seem to imply the same thing. As discussed in footnote 49, increasing bond polarity would not necessarily increase the net molecular dipole moment, for Y would be competing with H. There is some experimental evidence that the tetrahedral-to-trigonal Δr_{CY} decreases as the electronegativity of Y decreases. Thus C—Y bond strengthening and polarity increasing might still result in a lower net molecular dipole moment.

role of "electronegativity" with respect to intrinsic atomic polarity differences and environmental group polarity differences, and the connection with bond energies, is brought somewhat more into the open by the present simple model.

CONCLUSION

Effects customarily attributed to conjugation, hybridization, and group electronegativity can be rationalized to a remarkable extent in terms of nonbonded interactions. This suggests the foregoing factors are by no means as distinct from each other as they are often assumed to be. As a consequence it is improbable that unambiguous inferences of the nature of bonds in terms of these factors can be drawn from any set of experimental data, let along simple bond distances, until much more fundamental meanings are worked out. This conclusion is not really as pessimistic as it seems, for the model of nonbonded interactions that led to its formulation correlates a very extensive body of data in an extremely elementary way. Even in its present rudimentary form it is readily susceptible to the computation of numerical values of observables. If experience confirms the present proposal that intramolecular interactions between nonbonded atoms are comparable with intermolecular interactions at a given internuclear distance, such interactions *must* play a dominant role in the foregoing effects. If atoms are "whittled down" on the side of covalent bonds, nonbonded interactions may still often be of the same magnitude as the other interactions discussed.

Tetrahedron, 1962, Vol. 17, pp. 191 to 198. Pergamon Press, Ltd Printed in Northern Ireland

CONJUGATION, HYBRIDIZATION, AND STERIC HINDRANCE IN RELATION TO BOND LENGTHS*

E. BRIGHT WILSON, JR.
Mallinckrodt Chemical Laboratory, Harvard University Cambridge 38, Massachusetts

(*Received* 31 *January* 1961)

VOL. 17 1962

Abstract—Three theories which have been proposed to explain the observed shortening of a single bond when it is adjacent to a double bond are discussed. Possible predictions from these theories are examined, especially for comparison with various quantities measurable by microwave spectroscopy. It is concluded that the steric theory is probably untenable, that some conjugation appears necessary to explain observed barriers to internal rotation, and that it is difficult to find testable predictions from the hybridization theory.

IN theoretical chemistry various words have been introduced such as *conjugation*, *hybridization*, etc. which are used as the basis for explanations of certain empirical observations and generalizations. These explanations are sometimes only qualitative and sometimes semi-quantitative, but they never achieve anything approaching mathematical rigor and almost always have a heavy ingredient of parametric empiricism. This latter is often somewhat hidden from the casual observer.

It is therefore a fair question to ask about each of these words whether it represents a real physical concept or merely a psychologically consoling substitute therefore. In principle there is a simple test: does the concept lead with confidence to a substantial number of true predictions later successfully checked by experiment? The literature of chemistry is littered with the debris of discarded theories which provided satisfactory explanations of facts known at the time but which failed to predict correctly future facts—or just failed to predict.

Unfortunately, this test is simpler to state than it is to apply. Most of these concepts are sufficiently ill-defined so that their predictable consequences are usually subject to argument.

Recently various new experimental techniques, particularly microwave spectroscopy, have begun to yield data which are either of improved accuracy or of a qualitatively new type. These include more accurate bond lengths and bond angles, dipole moments and their components, change of dipole moment with vibrational state or isotopic substitution, barriers to internal rotation and some associated fine points, nuclear quadrupole coupling coefficients, molecular quadrupole moments, rotational magnetic moments, etc. It should be possible to use some of these to test the predictive power of some of our currently fashionable vocabulary.

THE ADJACENT BOND EFFECT

Rather than trying to cover all these items, this paper will concern itself primarily with a discussion of the observed fact[1] that a single bond adjacent to one or more multiple bonds is shorter than a single bond with only single bonds adjacent.

* The research reported in this paper was made possible by support extended Harvard University by the Office of Naval Research.

[1] G. Herzberg and B. P. Stoicheff, *Nature, Lond.* **175**, 79 (1955).

The object of the discussion will be to compare three current theories of this effect and to try to evaluate their respective power to predict other measurable quantities. Only qualitative arguments will be used.

It is perhaps first worthwhile to demonstrate the reality of the phenomena to be explained. Costain and Stoicheff[2] have reviewed the available data but several more recent examples can be added. Table 1 lists the lengths of some single bonds in various molecules whose structures have been determined by reasonably complete microwave studies with adequate isotopic substitution.

TABLE 1. LENGTHS OF SINGLE BONDS ADJACENT TO A DOUBLE BOND

Molecule	Bond	Length	Reduction
Propylene[a]	C—C	$1{\cdot}50_1$	$0{\cdot}02_5$*
Acetaldehyde[b]	C—C	$1{\cdot}50_1$	$0{\cdot}02_5$
Acetyl fluoride[c]	C—C	$1{\cdot}50_3$	$0{\cdot}02_3$
Acetyl chloride[d]	C—C	$1{\cdot}49_9$	$0{\cdot}02_7$
Acetyl cyanide[e]	C—C	$1{\cdot}49_6$	$0{\cdot}03_6$
Vinyl fluoride[f]	C—F	$1{\cdot}34_7$	$0{\cdot}03_7$†
Acetyl fluoride[c]	C—F	$1{\cdot}34_8$	$0{\cdot}03_6$
Vinyl chloride[g]	C—Cl	$1{\cdot}72_6$	$0{\cdot}05_{3}$‡
Acetyl chloride[d]	C—Cl	$1{\cdot}78_9$	$-0{\cdot}00_8$

* Compared with $1{\cdot}52_6$ in propane[h]
† Compared with $1{\cdot}38_1$ in CH_3F[i]
‡ Compared with $1{\cdot}78_1$ in CH_2Cl[j]
[a] D. R. Lide, Jr. and D. Christensen, to be published.
[b] R. W. Kilb, C. C. Lin and E. B. Wilson, *J. Chem. Phys.* **26**, 1695 (1957).
[c] L. Pierce and L. C. Krisher, *J. Chem. Phys.* **31**, 875 (1959).
[d] K. M. Sinnott, *J. Chem. Phys.* **34**, 851 (1961).
[e] L. C. Krisher and E. B. Wilson, *J. Chem. Phys.* **31**, 882 (1959).
[f] B. Bak, D. Christensen, L. Hansen-Nygaard and J. Rastrup-Andersen, *Spectrochim. Acta* **13**, 120 (1958).
[g] D. Kivelson, E. B. Wilson and D. R. Lide, *J. Chem. Phys.* **32**, 205 (1960).
[h] D. R. Lide, Jr., National Bureau of Standards Report 6802.
[i] C. C. Costain, *J. Chem. Phys.* **29**, 864 (1958).

Examination of Table 1 does show that single bonds are shortened when they are adjacent to multiple bonds, C—Cl in acetyl chloride being an apparent exception.

The principal theories of this effect might be called the steric hindrance, the hybridization, and the conjugation theories, respectively. Very plausible arguments have been put forward in support of each and a certain amount of controversy has been engendered.

STERIC HINDRANCE THEORY

The simplest theory is that of steric hindrance.[3,4] It is claimed that when three atoms are attached to each carbon at the end of a single bond, there is sufficient repulsion between the two sets of atoms to lengthen the single carbon–carbon bond beyond its "normal" length. When one carbon forms also a double or triple bond, it of course has one or two fewer atoms attached to it, so the steric repulsion tending to lengthen the single bond is reduced. Hence the single bond shortens, as is observed.

[2] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* **30**, 777 (1959).
[3] J. B. Conn, G. B. Kistiakowsky and E. A. Smith, *J. Amer. Chem. Soc.* **61**, 1868 (1939).
[4] Many others have supported this theory; e.g. L. S. Bartell, *J. Chem. Phys.* **32**, 827 (1960). See also A. Burawoy, *Trans. Faraday Soc.* **40**, 537 (1944).

VOL. 17 1962

This is an interesting picture which qualitatively explains the whole set of data on the shortening not only of single but also of double bonds as the number of attached atoms is diminished. However there are certain difficulties. In the first place it has to be said that extremely little is really known about the forces between non-bonded atoms within a given molecule. In many if not most cases there is at present no solid evidence as to whether the force is repulsive or attractive. However, the evidence from gas imperfections, compressibility of solids, and quantum mechanical theory all points to steric repulsion being a very steep function of distance. Consequently it would seem rather remarkable if different substituents did not have markedly different repulsions and hence a noticeably different effect on the C—C bond length.

The values of barriers to internal rotation about C—C bonds also do not appear to be compatible with the idea that there is strong repulsion between small atoms attached to the carbons. Table 2 gives some barrier values for ethane derivatives, all

TABLE 2. BARRIERS FOR ETHANE DERIVATIVES

Molecule	Barrier (kcal)
CH_3CH_3[a]	~2·8
CH_3CH_2F[b]	3·30
CH_3CHF_2[b]	3·18
CH_3CHCl[c]	3·56
CH_3CHBr[c]	3·57
CH_3CHI[d]	3·2
CH_3CHCN[e]	3·05

[a] K. S. Pitzer, *Disc. Faraday Soc.* **10**, 66 (1951).
[b] D. R. Herschbach, *J. Chem. Phys.* **25**, 358 (1956).
[c] D. R. Lide, Jr., *J. Chem. Phys.* **30**, 37 (1959).
[d] T. Kasuya, *J. Phys. Soc. Japan* **15**, 1273 (1960).
[e] V. W. Laurie, *J. Chem. Phys.* **31**, 1500 (1959).

the simple ethane derivatives whose barriers have so far been reported by microwave frequency methods. The relatively small variations of these values is noteworthy, suggesting that these barriers are not mainly due to steric repulsion. On the other hand, if atoms such as chlorine are substituted at each end there is fairly general belief that they do repel, at least when they are opposite one another. Normally they occupy a staggered conformation and then may or may not repel one another.

The crudest useful approximation for non-bonded repulsions is the rigid sphere model, e.g. Pauling's van der Waals radii,[5] such as form the basis for ordinary space-filling wooden ball atom models. In the bond directions these are of course flattened off at the appropriate covalent radius. This illustrates an important uncertainty of this approximation; namely the question of the way in which the radius should vary with the angle to the bond direction. There are probably numerous compounds in which two atoms attached to the same atom are closer together than the sum of their van der Waals radii but because of the angle, the area of overlap is small. One example is CH_2CCl_2, in which the Cl atoms are separated[6] by 2·90 Å whereas twice the van der Waals radius of Cl is 3·60 Å.

Bartell[4] has proposed that bond angles, at least about trigonal carbon, are largely determined by steric interference between pairs of attached atoms. He lists twenty-two

[5] L. Pauling, *Nature of the Chemical Bond* (3rd Ed.) p. 257. Cornell University Press, New York (1960).
[6] S. Sekino and T. Nishikawa, *J. Phys. Soc. Japan* **12**, 43 (1957).

molecules in which the angles are said to be predictable by this model. However, in evaluating this evidence it has to be remembered that the radii for X=C, H, F, and Cl were obtained from the compounds $H_2C{=}CX_2$, so these four do not provide a check. Similarly formic acid and urea were employed to give the oxygen and nitrogen radii. Further, the corresponding double ended molecules, such as F_2CCF_2, Cl_2CCCl_2 are

Table 3. Predictions of bond angles

Molecule	Angle	Obs.*	Calc.†	Δ‡	Δ§
CH_3CHO[a]	CCO	123° 55′	123° 10′	0° 45′	0° 30′
	OCH	118° 36′	124° 24′	−5° 48′	−4° 44′
	CCH	117° 29′	122° 27′	5° 2′	4° 19′
CH_3CFO[b]	CCO	128° 21′	125° 53′	2° 28′	4° 56′
	OCF	121° 21′	123° 14′	−1° 53′	−2° 4′
	CCF	110° 18′	110° 54′	−0° 36′	−2° 52′
CH_3CClO[c]	CCO	127° 5′	126° 47′	0° 18′	3° 40′
	OCCl	120° 16′	120° 42′	−0° 26′	−3° 9′
	CCCl	112° 39′	112° 32′	0° 7′	−0° 31′
CH_3CCNO[d]	H_3CCO	124° 3′	121° 37′	1° 86′	0° 38′
	OCCN	120° 58′	123° 23′	−2° 34′	−2° 27′
	CCCN	114° 59′	115° 0′	−0° 1′	1° 49′
CH_2CHCl[e]	CCCl	122° 18′	121° 42′	0° 36′	−1° 7′
	CCH	123° 49′	127° 2′	−3° 3′	0° 24′
	HCCl	113° 53′	111° 15′	2° 38′	0° 43′
HFCO[f]	FCO	122° 7′	122° 40′	−0° 33′	−1° 18′
	HCO	129°	122° 50′	6° 10′	5° 35′
	HCF	108°	114° 30′	−6° 30′	−5° 10′
H_2CCHCH_3[g]	CCC	124° 18′	122° 52′	1° 26′	0° 53′
	CCH	119° 0′	124° 58′	−5° 58′	−4° 25′
	HCC	116° 42′	112° 10′	4° 32′	3° 32′
H_2CCCl_2[h]	CCCl	123° 10′	(123° 21′)	−0° 7′	−0° 15′
	ClCCl	113° 40′	(113° 29′)	0° 11′	0° 30′
Root-mean-square				3·2°	3·3°

* Precision perhaps ±30′
† Calculated with Bartell model
‡ Obs.-calc.
§ Obs.-123° 25′ or obs.-113° 10′

[a] R. W. Kilb, C. C. Lin and R. B. Wilson, *J. Chem. Phys.* **26**, 1695 (1957).
[b] L. Pierce and L. C. Krisher, *J. Chem. Phys.* **31**, 875 (1959).
[c] K. M. Sinnott, *J. Chem. Phys.* **34**, 851 (1961).
[d] L. C. Krisher and E. B. Wilson, Jr., *J. Chem. Phys.* **31**, 882 (1959).
[e] D. Kivelson, E. B. Wilson and D. R. Lide, *J. Chem. Phys.* **32**, 205 (1960).
[f] O. H. LeBlank, Jr., V. W. Laurie, and W. D. Gwinn, *J. Chem. Phys.*, **33**, 598 (1960).
[g] Private communication, D. R. Lide and D. Christensen, to be published.
[h] S. Sekino and T. Nishikawa, *J. Phys. Soc. Japan* **12**, 43 (1957).

not really independent. Some of the other molecules listed have not yet been adequately studied experimentally.

Table 3 shows the results of applying this theory to some molecules with trigonal carbon whose structures have been determined by microwave spectroscopy using an adequate number of isotopes. Column 5 shows the deviations between the observed angles and those calculated with Bartell's method, using his radii. The root-mean-square deviation is 3·2° (calculated using the two independent angles for each molecule). However, examination of the data shows that angles between a double bond

and a single bond tend to be somewhat larger than 120° and those between two single bonds somewhere around 113°. The last column of Table 3 shows the deviations between observations and prediction when it is predicted that all angles between a single and a double bond (to carbon) are the same, namely 123° 25′ while all single–single bond angles are therefore predicted to be $360° - 2 \times 123° 25' = 113° 10'$. The standard deviation here is 3·3° (on the same basis as above). So it seems that one can predict angles essentially as well with this simple theory with one empirical adjustable parameter as with the more elaborate one with six empirical radii. (Note that the six parameters were not, however, evaluated from these molecules.) The fact is that this steric model accomplishes nothing more than dividing the angles into the two classes, which it does because of the shortness of a double bond compared with a single bond. It does not successfully predict even the rank order within each class.

VOL. 17 1962

If steric repulsions do not appear to be important in determining variations in bond angles, they are even less likely to cause variations in bond lengths, for which the force constants are much larger than for angles. Consequently, the theory that bond shortening is due to the relief of steric repulsion seems not very likely, even though our ignorance of these forces is so great that it perhaps cannot be completely ruled out.

HYBRIDIZATION THEORY

The hybridization theory[7] is based on a particular picture of the nature of the orbitals used in forming single, double and triple bonds. If carbon forms four single bonds, Pauling's picture calls for each to be a hybrid of *s* and *p* and all alike, so each is a so-called sp^3 type. For double bonds there is an apparent choice. One picture has the double bond formed from two single bonds, as in the sharing of edges of a tetrahedron.

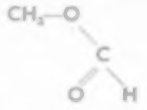
Here all bonds might still be tetrahedral and, incidentally, if the orbital angles remained at the tetrahedral value 109° 28′, the single–double bond angle would be 125° 16′, not far from the average value observed for such angles in Table 3. On the other hand, the more usual picture is that the *s* and two of the three *p* orbitals are hybridized to form three equivalent bonds in a plane, so-called sp^2 or trigonal bonds, making an angle of 120° with one another. The third *p* orbital is perpendicular to the plane of the other orbitals. The double bond is then formed by the overlap of a trigonal orbital from each carbon, directed toward the other carbon, and by the interaction of the two *p* (here called π) orbitals.

This picture will change the hybridization and, it is agreed, therefore the length of the single bonds on the same carbon as the double bond.

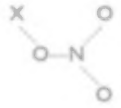
This picture would seem to require that other single bonds to carbon suffer a similar shortening. It is true that C—H bonds seem to diminish in length from ethane through ethylene to acetylene. However, it has to be pointed out that bond lengths involving hydrogen are the most uncertain experimentally because of the low scattering power of hydrogen for electrons and X-rays, the small contribution to moments of inertia, and the large amplitude of motion. Further, the shortening is only about 0·03 Å from ethane to acetylene whereas the carbon–carbon bond diminishes by nearly 0·07 Å from propane to methyl acetylene. Consequently, the idea of a carbon *radius* dependent only on hybridization is qualitatively but not quantitatively acceptable.

[7] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

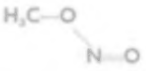
When the single bond from carbon connects an atom with one or more unshared pairs and also one or more additional bonds, such as can be the case with oxygen or nitrogen, the single bond again is reduced in length when adjacent to a double bond, but in this case it is possible to demonstrate that the shortening cannot be due to a change in hybridization alone. Consider for example the case of methyl formate



whose structure was carefully studied by Curl[9]. The single bond O—C= is 1·334 Å compared with $1{\cdot}43_7$ Å for O—C— so considerable shortening has occurred. However, all the atoms except CH_3 hydrogens are held in a plane, apparently rather firmly despite the real possibility of steric repulsion between the H's on CH_3 and the carbonyl oxygen. A similar result, which however involves nitrogen and not carbon, occurs with nitric acid[9] and with methyl nitrate.[10]



Here it is now well proven, contrary to earlier electron diffraction results,[11] that X = H or CH_3 lies in the plane of ONO_2 with a considerable barrier of the order of 9 kcal[12,13] interfering with rotation about the XO—N bond. Likewise NMR[14] data on methyl nitrite



give a considerable barrier for rotation about the middle bond. Acoustic absorption data[15] in the liquid phase also yields a barrier exceeding 5 kcal for single bonds adjacent to double bonds in the following molecules: acrolein, crotonaldehyde, cinnamaldehyde, methacrolein and furacrolein.

CONJUGATION AND HYPERCONJUGATION

These considerable barriers are not simply predictable from the change in hybridization alone. On the other hand, the conjugation theory[16] accounts for them nicely. According to this theory, there is resonance between the structures

In the latter, charge has migrated to the extreme carbon from an orbital on oxygen formerly filled with an unshared pair. The C—O bond then takes on a partial double

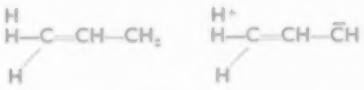
[9] R. F. Curl, Jr., *J. Chem. Phys.* **30**, 1529 (1959).
[10] D. J. Millen and J. R. Morton, *J. Chem. Soc.* 1523 (1960).
[11] W. Dixon and E. B. Wilson, Jr., *J. Chem. Phys.* **35**, 191 (1961).
[12] L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.* **59**, 13 (1947).
[13] H. Cohn, C. K. Ingold and H. G. Poole, *J. Chem. Phys.* **24**, 162 (1956).
[14] A. Palm and M. Kilpatrick, *J. Chem. Phys.* **23**, 1562 (1955).
[15] L. H. Piette and W. A. Anderson, *J. Chem. Phys.* **30**, 899 (1959)
[16] M. S. de Groot and J. Lamb, *Proc. Roy. Soc.* A **242**, 36 (1957).
[16] See ref. 5, esp. Chap. 8.

bond character and is accordingly both shortened and endowed with considerable resistance to twisting.

Another type of evidence is available in case the attached atom has a nuclear electrical quadrupole moment. For example, in vinyl chloride[17,18] it is possible to measure a fine structure in the microwave spectrum due to the interaction of the chlorine nuclear quadrupole moment with the gradient of the electric field at the chlorine nucleus arising from the electrons and especially the outer shell electrons. The results show that the field gradients are not the same in the two directions perpendicular to the C—Cl bond, whereas a pure single bond would be expected to be cylindrically symmetrical. Orbital arguments[19] lead to a double bond character of about 6 per cent. The C—Cl bond is also shorter than in CH_3Cl, for example.

VOL. 17 1962

In case the single bond connects an atom without unshared pairs, e.g. carbon, the question is somewhat more open (unless of course the bonds are part of a fully conjugated system such as in benzene). Without lone pairs it is necessary to invoke *hyperconjugation*,[20] a concept rather less esthetically appealing to many. Thus in propylene $CH_3HC{=}CH_2$ it is assumed that structures such as



contribute, in addition to the normal structure. It is difficult to obtain the same kind of evidence. Carbon does not have any nuclear electrical quadrupole moment. Further, hyperconjugation with a methyl group will not influence the three fold barrier to internal rotation ordinarily measured. However, it should contribute to the sixfold part of the barrier, but the amount to be expected would probably be very difficult to estimate because it would depend on the sixth order term in the Fourier expansion of the twofold components and that would depend in turn rather delicately on the barrier shape.

All these forms of conjugation imply a transfer of charge in the molecule which is the greater the more important is the conjugation. Consequently, if a distortion of the molecule is made which favors one or the other of the resonating forms, the dipole moment should be changed in a predictable direction by an amount depending on the amount of conjugation. This should appear as especially strong contributions to the intensity of certain infrared absorption bands. It may be possible to detect an effect of this kind in another way. In certain cases the average dipole moment should change with vibrational state. An example which has been partially examined is methyl nitrate in which one might expect the conjugation to be diminished by twisting the NO_2 group out of the plane. Since this effect should cause a charge to be transferred along the axis of twist, it should not average out over a cycle of the twisting motion but should change the dipole moment as the torsional state is changed. To about 1 per cent no change is experimentally observed up through the second excited state but crude calculations suggest that no effect larger than 1 per cent should be observed until a higher excited state is reached. It should be possible to look for this effect

[17] J. H. Goldstein and J. K. Bragg, *Phys. Rev.* **75**, 1453 (1949).
[18] D. Kivelson, E. B. Wilson and D. R. Lide, *J. Chem. Phys.* **32**, 205 (1960).
[19] J. H. Goldstein, *J. Chem. Phys.* **24**, 106 (1956).
[20] See for example R. S. Mulliken, *Tetrahedron* **5**, 253 (1959).

with some refinements in technique.* It has been pointed out[21] that conjugation should also make a large positive contribution to the interaction force constant between the stretching of the two bonds with double bond character. However, such constants are difficult to determine.

It is more difficult to find possible experimental indicators of hybridization. One which is often invoked is the value of the bond angle. Unfortunately it is easy to find examples which show that this is not a simple indicator. Thus in tetrahedral carbon if the angle between one pair of bonds is opened up the opposite angle should close down,[22] if hybridization is the sole determinant of bond angle and only *s,p* orbitals are used. Instead, in CH_2Cl_2 both angles[23] open up. This is of course explanable in terms of "bent bonds" but once this additional concept is added to that of hybridization, the whole picture hardly satisfies Platt's requirement that "a theory must be capable of being disproved".

CONCLUSION

Despite the additional information provided by microwave spectroscopy it does not seem possible as yet to decide for certain whether a single bond next to a double bond is shortened because of relief of steric repulsion, change of hybridization, or conjugation. Nevertheless arguments are presented which make the steric theory seem the least important contributor whereas the data seem to indicate that some appreciable contribution from conjugation is required. A change in hybridization cannot be ruled out but seems unlikely to be the sole phenomena responsible, a conclusion in agreement with that of others.[24,25]

* D. R. Lide, Jr., *J. Chem. Phys.* **33**, 1879 (1960) points out also that a knowledge of the *components* of the dipole moment, determinable from microwave spectroscopy, seems to support a hyperconjugation rather than a hybridization basis for the dipole in propylene.

[21] C. A. Coulson, J. Duchesne and C. Manneback, *Victor Henri Memorial Volume*. Desoir, Liege (1948).
[22] C. A. Coulson, *Valence*. Clarendon Press, Oxford (1952).
[23] R. J. Myers and W. D. Gwinn, *J. Chem. Phys.* **20**, 1420 (1952).
[24] R. S. Mulliken, *Tetrahedron* **6**, 68 (1959).
[25] B. Bak and L. Hansen-Nygaard, *J. Chem. Phys.* **33**, 418 (1960).

Tetrahedron, 1962, Vol. 17, pp. 199 to 214. Pergamon Press, Ltd. Printed in Northern Ireland

ELECTRON DONOR AND ACCEPTOR PROPERTIES OF ALKYL SUBSTITUENTS

W. M. SCHUBERT,[1] R. B. MURPHY and J. ROBINS
Department of Chemistry of the University of Washington

(*Received* 9 *January* 1961)

VOL. 17 1962

Abstract—The polar effects of alkyl substituents in electrophilic and nucleophilic chemical and electronic transitions is discussed. The question of the importance of hyperconjugation in the electron donor properties of alkyl substituents is raised. In view of the cogent arguments of Dewar, it is doubtful whether quantum mechanical calculations embodying hyperconjugation constitute proof of this effect. That the art of quantum mechanics may not yet be sufficiently developed to be used as proof for or against secondary resonance effects also is evidenced by the calculations of Simpson, who found that an internal dispersion force model (in which conjugation was neglected) reproduced the properties of butadiene just as satisfactorily as the models embodying conjugation. The *experimental* facts do not unequivocally support the hyperconjugation hypothesis and indeed are, at least in part, contradictory to it. In particular, the demonstration that the Baker–Nathan Effect[2] may be due to the influence of alkyl substituents on the differential solvation of ground and transition states casts doubt on the interpretation that this experimental effect is due to a dominant role of C-H hyperconjugation.

In nucleophilic chemical reactions, rate or equilibrium constants for *para* (or *meta*) alkyl derivatives are somewhat smaller than those of the corresponding hydrogen compounds. A number of authors have interpreted this in terms of a permanent electron donor role of alkyl substituents (e.g. by hyperconjugation) relative to the hydrogen substituent. However, this static viewpoint of substituent effects fails to account for the finding that *p*-alkyl substituents function as apparent electron acceptors (relative to the *p*-hydrogen substituent) in appreciably lowering the energy of the nucleophilic principal electronic transition of phenol, anisole, aniline and N,N-dimethylaniline. These results are qualitatively rationalized in terms of "substituent-polarizability" and electronegativity.

The *p*-neopentyl substituent lowers the energy of both electrophilic and nucleophilic electronic transitions to an appreciably greater extent than either the *p*-methyl or *p*-*t*-butyl substituent. This extra stabilizing effect of the neopentyl substituent on both electron deficient and electron rich centers may be due to an internal dispersion force interaction, since the geometry of the neopentyl compounds is particularly favorable for such an interaction.

IN recent years the electronic effect of alkyl substituents in chemical and electronic transitions has undergone a thorough reappraisal. The role of alkyl substituents as electron donors has received by far the most study and attention, and the first part of this paper discusses the current status of the role of alkyl substituents as apparent electron donors toward electron-demanding unsaturated systems. In the second part of this paper data is presented which shows that under suitable conditions alkyl substituents may also function as apparent electron acceptors relative to the hydrogen substituent. A qualitative empirical treatment of polar effects of alkyl substituents in terms of substituent electro-negativity and "substituent-polarizability" is presented.

ALKYL GROUPS AS APPARENT ELECTRON DONORS

The many viewpoints and postulates regarding the electron donor properties of alkyl substituents seem to be roughly divisible into two categories, a "hyperconjugative

[1] John Simon Guggenheim Fellow at the Laboratorium für Physikalische Chemie und Elektrochemie der Technischen Hochschule, Stuttgart, Germany, 1960–1961.

category" and an "inductive effect category". However, variations of viewpoint within each of these categories are many, and all shades of meaning between the two categories can be read into the many words written about alkyl substituent effects. The founders of the hyperconjugation viewpoint are Baker and Nathan, who first postulated hyperconjugation (C—H) in 1935 to account for the Baker–Nathan Effect in chemical reactions in which the alkyl substituent is presumably strongly called upon to release electrons.[2-5] Among quantum mechanicians, the prime proponent of hyperconjugation is Mulliken, who has carried out numerous LCAO-MO calculations based on an acetylenic or ethylenic model for the alkyl group (e.g. $H_3{\equiv}C{-}X{=}Y$ or $R_3{\equiv}C{-}X{=}Y$, in which one of the bonds to the H_3 or R_3 group is considered as a pseudo σ bond, labeled $[\sigma]$, and the other two bonds are considered as pseudo-π, labeled $[\pi_x]$ and $[\pi_y]$.[6-9] A similar model is used by Coulson[10]. Other models include those in which a methyl group is treated as a single heteroatom.[11,12] Kreevoy and Eyring, in order to explain what they considered to be the particular effectiveness of α-hydrogens on the alkyl group, used an "α-hydrogen bonding" model in which is employed a non-zero resonance integral of the α-hydrogen 1s orbital with the π-orbital of the unsaturated system.[13]

The inductive viewpoint in its extreme was expressed by Burawoy, who advocated the idea that π-electron resonance is non-existent.[14] In keeping with this idea Burawoy and Spinner assumed a purely inductive mechanism for electron release by alkyl groups.[15]

Dewar considers the evidence for delocalization of bonds in polyenes (e.g. butadiene), olefins (e.g. propylene) and acetylenes (e.g. methylacetylene) to be inconclusive, and has concluded that "resonance is important only in molecules for which more than one classical (unexcited) structure can be written". All observable effects in the ground states of conjugated and hyperconjugated molecules, such as "stabilization energy",[16] shortenings of single bond distances (e.g. the carbon–carbon single bond of butadiene and methylacetylene) and polarities (e.g. of propylene) are ascribed to changes in carbon–carbon σ bond hybridization.[17] However, these conclusions were considered not necessarily applicable to excited electronic states or to transition states of the reactions of such molecules. Mulliken, in arguing against the Dewar proposals and

[2] The term Baker–Nathan Effect is used here in its experimental sense; that is, it refers to a tendency for observed energies or heats of electron-demanding transitions to take the order $CH_3 < Et < iPr < tBu$, or for rate or equilibrium constants to take the order $CH_3 > Et > iPr > tBu$.

[3] The term "hyperconjugation" for the delocalization of σ-bonds to saturated carbon first appeared in a publication by Mulliken and was suggested by W. G. Brown.[6,7]

[4] J. W. Baker *Hyperconjugation*, Oxford University Press, London (1953).

[5] Conference on Hyperconjugation, *Tetrahedron* **5**, 105–274 (1959).

[6] R. S. Mulliken, *J. Chem. Phys.* **7**, 339 (1939).

[7] R. S. Mulliken, C. A. Riecke and W. G. Brown, *J. Amer. Chem. Soc.* **63**, 41 (1941).

[8] R. S. Mulliken, *Tetrahedron* **5**, 253 (1959).

[9] R. S. Mulliken, *Tetrahedron* **6**, 68 (1959).

[10] C. A. Coulson, *Valence*, pp. 307–317. Oxford University Press, London (1952).

[11] F. A. Matsen, *J. Amer. Chem. Soc.* **72**, 5243 (1950).

[12] A. Streitwieser, Jr. and P. M. Nair, *Tetrahedron* **5**, 149 (1959).

[13] M. M. Kreevoy and H. Eyring, *J. Amer. Chem. Soc.* **79**, 5121 (1957); M. M. Kreevoy, *Tetrahedron* **5**, 233 (1959).

[14] A. Burawoy, *Trans. Faraday Soc.* **40**, 537 (1944); *Victor Henri Memorial Volume*. Desoer, Liége (1948).

[15] A. Burawoy and E. Spinner, *J. Chem. Soc.* 3752 (1954).

[16] Dewar has suggested the term "stabilization energy" to be used in place of "resonance energy" for the observed extra thermodynamic stability of conjugated molecules compared with unconjugated analogues.[17]

[17] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959); *Ibid.* **11**, 96 (1960).

VOL. 17 1962

for an important role of π-electron delocalization in "ordinary" conjugated or hyperconjugated molecules seems to rely mainly on the fairly consistent agreement of a number of quantum mechanical calculations.[8,9] However, he concedes that "Dewar's challenge has in any event made clear the importance of a careful re-examination of the theoretical basis of conjugation, hyperconjugation and related phenomena".[9]

Simpson also has raised the question of the relative importance of conjugative interaction in butadiene and higher polyenes. Neglecting resonance interaction altogether, he carried out quantum mechanical calculations based on a dispersion force model for butadiene which satisfactorily reproduced the stabilization energy and positions of singlet–singlet absorption bands and accounted for bond length alternations.[18] Internal dispersion force interactions also are given considerable weight in the calculations of Berry[19].

The experimental chemist finds himself somewhat at a loss to evaluate to what extent the necessarily approximate quantum mechanical calculations based on various models can alone be used as arguments for or against specific effects such as hyperconjugation. However, the viewpoints expressed by Dewar and the calculations of Simpson have at least given cause for reflection as to whether the quantum–mechanical "evidence" for hyperconjugation is sufficiently convincing. The need of a theory of hyperconjugation to explain certain *experimental observations* seems to be no longer as urgent as once thought to be since these observations are now also subject to different interpretations.

Chief among the experimental observations cited in support of the theory of hyperconjugation has been the Baker–Nathan Effect.[2] This effect, which is usually found in chemical transitions that call strongly upon the substituent for electron release, has until recently been universally interpreted as showing net electron release in the order Me > Et > iPr > tBu and hence as meaning that C—H hyperconjugation is the main mechanism of electron release in these instances.[20] However, this interpretation has been seriously questioned.[22–25]

By and large there has been a tendency to take experimental results such as orders of rate constants or equilibrium constants at face value; that is, to view transitions in solution as if they were taking place in the gas phase. The possible effect of alkyl substituents on the solvent stabilization of the states in a transition usually has been omitted altogether from consideration, and in other instances dismissed with varying degrees of arbitrariness as being of secondary importance.[8,21,26] However, the research groups of Shiner[27] and Schubert[22–25] have found the Baker–Nathan Effect to be solvent dependent, in a manner not explainable by the original theory of Baker and

[18] W. T. Simpson, *J. Amer. Chem. Soc.* **73**, 5363 (1951).
[19] R. S. Berry, *J. Chem. Phys.* **26**, 1660 (1957); *Ibid.* **30**, 936 (1959).
[20] Berliner has listed some forty reactions in which the Baker–Nathan Effect is found and has concluded primarily from the mere persistence of this effect that "hyperconjugation of C—H bonds provides the most consistent and satisfactory explanation".[21]
[21] E. Berliner, *Tetrahedron* **5**, 202 (1959).
[22] W. M. Schubert and W. A. Sweeney, *J. Org. Chem.* **21**, 119 (1956); *J. Amer. Chem. Soc.* **76**, 4625 (1954).
[23] W. M. Schubert, J. Robins and J. L. Haun, *J. Amer. Chem. Soc.* **79**, 910 (1957); [b] W. M. Schubert and J. Robins, *Ibid.*, **80**, 559 (1958); [c] W. M. Schubert, J. Robins and J. M. Craven, *J. Org. Chem.* **24**, 943 (1959).
[24] W. M. Schubert, J. M. Craven, R. Minton and R. B. Murphy, *Tetrahedron* **5**, 194 (1959).
[25] W. M. Schubert and R. Minton, *J. Amer. Chem. Soc.* **82**, 6188 (1960).
[26] R. W. Taft, Jr. and Irwin C. Lewis, *Tetrahedron* **5**, 210 (1959).
[27a] V. J. Shiner, Jr., *J. Amer. Chem. Soc.* **76**, 1603 (1954); [b] *Tetrahedron*, **5**, 243 (1959); [c] V. J. Shiner, Jr. and C. J. Verbanic, *J. Amer. Chem. Soc.* **79**, 369 (1957).

Nathan, and have suggested specific roles of the solvent. These groups were led independently to a consideration of the solvent role through a recognition of the fact that the Baker–Nathan Effect, though often observed in electron-demanding chemical reactions, is rarely encountered in measurements on other electron-demanding transitions, e.g., in the ionization potentials and "principal" electronic excitation energies of alkyl-unsaturated compounds.[22–25,28] The Baker–Nathan Effect also is not found in ground state measurements such as dipole moments,[31] bond lengths[32] and heats of hydrogenation.[33] This inconsistency between the Baker–Nathan Theory and experimental fact also was recognized by Burawoy and Spinner.[15] They neglected the possible role of the solvent, however, and attributed the Baker–Nathan Effect to "steric hindrance to bond shortening" in purely inductive electron release by alkyl substituents. The absence of the Baker–Nathan Effect in highly electron demanding electron transitions was explained in terms of the Franck–Condon Principle; that is, in the short time of the electronic excitation process there is practically no movement of atomic nuclei, hence practically no bond shortening.[15] However, the hypothesis of Burawoy and Spinner does not satisfactorily account for the solvent dependence of the Baker–Nathan Effect in both chemical and electronic transitions.

Schubert and Sweeney maintained that alkyl substituents stabilize electron-demanding unsaturated systems in the inductive order, regardless of whether the substituent is faced with a large or small electron deficiency. They postulated that the Baker–Nathan Effect is due to steric hindrance to solvation near bulky alkyl groups; that is, that the solvent stabilization of alkyl unsaturated compounds is significantly decreased with increasing ability of the alkyl substituent to shield electron deficient sites in its vicinity.[22] This hypothesis leads to many of the same qualitative predictions for chemical reactions in solution as the hypothesis of Baker and Nathan, e.g. that the Baker–Nathan Effect should be observed when the electron deficiency (and hence the requirement for solvation) created in that part of the reacting molecule containing the substituent is large.[34] On the other hand, observations made on electronic transitions,[22,24] such as the inductive order of the principal electronic transition energies of *p*-alkyl nitrobenzenes and acetophenones in the gas phase and, the partial inversion of this order in polar basic solvents,[23a] are consistent with the hypothesis of Schubert and Sweeney and inconsistent with the hypothesis of Baker and Nathan. The fact that the solvent molecules are not fully oriented to the electronic excited states (Franck–Condon Principle) accounts for the mildness of the Baker–Nathan Effect in this particular instance and for its rare appearance in electron-demanding electronic transitions in

[28] A hyperconjugative order of excitation energies in the gas phase has been found only for the low intensity "B-band" of alkyl benzenes at ca. 2600 Å (but not for the intense polar "principal" or "E-band" transition at ca. 2100 Å).[29] What the substituent is called upon to do in this "almost non-polar transition"[30a] is not entirely clear. The interpretation that the energy order is due to predominant C—H hyperconjugation in the excited state[29] has been questioned and other explanations have been advanced.[30]

[29] F. A. Matsen, W. W. Robertson and R. L. Choake, *Chem. Rev.* **41**, 273 (1947).

[30a] K. Bowden and E. A. Braude, *J. Chem. Soc.* 1068 (1952); [b] V. J. Hammond, W. C. Price, J. P. Teegan and A. D. Walsh, *Disc. Faraday Soc.* **9**, 53 (1950).

[31] C. P. Smyth, *Dielectric Behavior and Structure* Chaps. IX and X. McGraw-Hill, New York (1955).

[32] Sutton has concluded that "hyperconjugation is not clearly and ambiguously proved by bond length anomalies to exist in the ground state of molecules, although on the other hand its existence is not certainly disproved". L. E. Sutton, *Tetrahedron* **5**, 118 (1959).

[33] Turner has concluded that thermochemical results do not provide significant information on the nature of the stabilization of unsaturated systems by alkyl groups (see, however, ref. 26); R. B. Turner, *Tetrahedron* **5**, 141 (1959).

[34] A typical example is the solvolysis of *p*-alkyl benzhydryl chlorides, for which the latter hypothesis, however, accounts more satisfactorily for the order of observed activation entropies.[22,35]

solution in general.[22-24] Qualitatively considered, these results also are consistent with Shiner's suggestion that the solvent, through incipient hydrogen bonding with the α-hydrogens of the alkyl substituent, may function to enhance C—H over C—C hyperconjugation.[27] Quantitatively considered, the solution data for the *p*-alkyl nitro-benzenes and acetophenones were better accomodated by the hypothesis of steric hindrance to solvation near bulky alkyl groups.[23a]

Most recently it has been found that the kinetic parameters (k, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the solvolysis of 3-R- and 3,5-diR-benzhydryl chlorides (R = H, CH_3, and t-Bu) vary with solvent composition and substituent in a manner consistent with the hypothesis of Schubert and Sweeney, and inconsistent with the Baker–Nathan hypothesis, either as originally enunciated or as modified by Shiner.[25] Support for the steric hindrance to solvation argument was also found by Clement and co-workers in the solvation energies of benzyl, *p*-methylbenzyl and *p*-t-butylbenzyl chlorides in methanol, determined from vapor pressures of the pure chlorides and the Henry's law constants in solution.[25] Earlier, Shiner had found that the Baker–Nathan Effect in the solvolysis of *p*-alkylbenzhydryl chlorides is solvent dependent and concluded that the variations in relative rates with solvent composition could be explained in terms of solvent assistance to hyperconjugation or steric hindrance to solvation, or both.[27e]

In view of the above considerations it is the contention of the authors that the appearance of the Baker–Nathan Effect in transitions in solution does not constitute evidence for a C—H hyperconjugative order of electron release by alkyl substituents. If this contention is correct, then C—H hyperconjugation would have to yield in importance to stabilization mechanisms in the inductive order, such as the inductive effect itself, or internal dispersion forces,[18] or C—C hyperconjugation. It is a moot question whether hyperconjugation in general (both C—C and C—H) is important, although the postulate that it is a major factor seems now to offer no special advantage.

In connection with the question of the total electron donor effect of alkyl substituents, it is interesting to note that there has been a recent tendency among those favoring the hyperconjugation viewpoint to de-emphasize the relative importance of C—H hyperconjugation and to assign to C—C hyperconjugation an important, though generally lesser role. Thus Mulliken, who suggests the term "differential hyperconjugation" for use in discussions of the Baker–Nathan Effect, sees "no obvious reason" why C—C hyperconjugation "should be radically different in its effectiveness" than C—H hyperconjugation.[8] In fact, Mulliken early made no distinction between C—H and C—C hyperconjugation.[6,7] Perhaps the first to explicitly apply C—C hyperconjugation, in a qualitative way, are Berliner and Bondhus, who held that the rate of molecular bromination of t-butyl benzene relative to benzene ($k_{tBu}/k_H = 115$ for "total" bromination at 25°) is too great to be attributable to the inductive effect alone and hence must be determined considerably by C—C hyperconjugation.[36] However, as de la Mare has pointed out, this is still a matter of opinion.[37] Recently, varying degrees of effectiveness have been assigned to C—C hyperconjugation, up to a ratio of C—C to C—H hyperconjugation of about 0·8.[26,38] It is to be emphasized that

[25] R. A. Clement, J. N. Naghizadeh and M. R. Rice, *J. Amer. Chem. Soc.* **82**, 2449 (1960); R. A. Clement and J. N. Naghizadeh, *Ibid.* **81**, 3154 (1959).

[36] E. Berliner and F. J. Bondhus, *J. Amer. Chem. Soc.* **70**, 854 (1948).

[37] P. B. D. de la Mare, *Tetrahedron* **5**, 107 (1959).

[38a] P. D. Bartlett, *J, Chem. Educ.* **30**, 29 (1953); N. N. Lichtin and P. D. Bartlett, *J. Amer. Chem. Soc.* **70**, 854 (1948); [b] H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *J. Amer. Chem. Soc.* **79**, 1897 (1957).

VOL. 17 1962

these "quantitative" estimations are based on rate constants in solution and neglect the possible effect of differential solvation on k_{CH_3}/k_{tBu} ratios.

ALKYL GROUPS AS APPARENT ELECTRON ACCEPTORS

I. *Introduction*

The amount of theorizing and experimental study that has been devoted to the influence of alkyl substituents on nucleophilic, i.e. electron rich, centers is much less than that given to the influence of alkyl substituents on electrophilic, i.e. electron

TABLE 1. NUCLEOPHILIC REACTIONS OF *p*-ALKYL COMPOUNDS

Ref.	Reaction	Solvent	Temp.	Relative rate constants H	Me	t-Bu	ρ Values[a]
41a	Ethylbenzoates + OH^-	85% EtOH[b]	25°	1	0·44	0·56	2·5
41a	Ethylbenzoates + OH^-	56% Acetone[b]	25°	1	0·41	0·31	2·3
42[c]	*l*-menthylbenzoates + OCH_3^-	CH_3OH	40°	1	0·48	0·59	2·6
41b	Neutral hydrolysis of benzoic anhydrides	75% Dioxane[b]	58°	1	0·35	0·39	1·6
43	Ethanolysis of benzoyl chlorides	EtOH	0°	1	0·57	0·67	1·5
43	Benzylpyridinium ions + OEt^-	EtOH	20°	1	0·50	0·69	—
43	2-Cl-5-alkyl-3,5-dinitrobenzenes + piperidine	Piperidine	50°	1	0·18	0·31	—
41c[d]	2-Bromo-5-alkylnitrobenzenes + piperidine	Piperidine	25°	1	0·15	0·17	4·9

[a] Values of the reaction constant, ρ, are taken either from the original reference or from ref. 40.
[b] Given as percentage by weight of aqueous solution.
[c] Activation energies obtained from rate constants at two temperature are 17·6, 18·0 and 18·1 for *p*-H, *p*-CH_3 and *p*-t-Bu compounds respectively. It was cautioned that these values may be somewhat in error.[42]
[d] Activation energies obtained from rate constants at two temperatures are 12·1 ± 0·8, 13·2 ± 0·6 and 12·9 ± 0·4 for *p*-H, *p*-CH_3 and *p*-t-Bu compounds respectively.

deficient, centers. Nevertheless, rate or equilibrium constants have been determined for *p*-alkyl compounds in a number of nucleophilic chemical reactions in which negative charge is fed toward the substituent. Most of the reactions in which *para* hydrogen, methyl and t-butyl compounds have been compared are listed in Table 1. These reactions have a positive value of the Hammett reaction constant, ρ. The rate constants are somewhat smaller for the *p*-alkyl derivatives than for the corresponding *p*-hydrogen compounds, in agreement with the negative sign of the substituent constants, σ, assigned to alkyl substituents.[39,40]

[39] L. P. Hammett, *Physical Organic Chemistry* Chap. VII. McGraw-Hill, New York (1940).
[40] H. H. Jaffé, *Chem. Rev.* **53**, 191 (1953).

VOL. 17 1962

In the discussions of the deactivating effect of alkyl substituents relative to the hydrogen substituent in nucleophilic reactions, a static viewpoint has been taken. That is, the alkyl group is treated as a permanent electron donor relative to hydrogen, i.e. it is considered as resisting negative charge, and the usual discussions of hyperconjugative vs. inductive electron release are applied.[41–43] In most of these nucleophilic reactions, the rate or equilibrium constant is slightly smaller for the *p*-methyl than for the *p*-t-butyl derivative. This has been attributed to hyperconjugation, that is to an electron release order governed by C—H hyperconjugative electron release.[41–43] There is a certain inconsistency between this argument and that applied to electrophilic reactions. For electrophilic reactions, it is maintained that C—H hyperconjugative electron release should predominate over inductive electron release only when the electron *demand* placed upon the substituent is high. Why C—H hyperconjugative electron *release* should predominate in nucleophilic reactions, in which the electron demand placed upon the substituent is negative, is not altogether clear. Actually, there is no assurance that the very small differences between the rate or equilibrium constants of the methyl and t-butyl compounds reflect differences in the direct potential energy effects of the methyl and t-butyl substituents, or indeed, that these rate or equilibrium constant differences are due to differences in heats of activation or entropies of reaction. Heats and entropies of activation were determined for but two of the reactions of Table 1, but in these instances the values obtained are not reliable enough to permit a definite conclusion to be made. Furthermore, it is not known to what extent differential solvation of ground and excited states may influence the relative rates of the compounds of Table 1. That differential solvation may be a factor is evidenced by the inversion of the rate order for *p*-methyl and *p*-t-butyl compounds in the basic hydrolysis of ethyl benzoates in "56%" acetone as compared to "85%" alcohol.[44] In the absence of accurate heat and entropy data for the reactions of Table 1 it may be premature to attribute the small rate or equilibrium constant differences between the *p*-methyl and *p*-t-butyl compounds to differences in the direct polar effects of the substituents. Presumably, the larger rate or equilibrium constant differences between the *p*-alkyl and *p*-hydrogen compounds do qualitatively follow the differences in the polar effects of *p*-alkyl and *p*-hydrogen substituents in these instances, although this is not altogether certain.

The consideration of alkyl substituents as permanent electron donors relative to hydrogen is a manifestation of a prevalent static viewpoint of substituent effects in general; i.e. the electrical influence of substituents are treated in terms of mesomeric and inductive effects in fixed directions. Contributing toward the crystallization of a static viewpoint of substituent electronic effects has been the assignment to substituents of σ-values of constant sign, if not of constant magnitude. Thus, a negative σ is taken as implying permanent net electron release relative to hydrogen and a positive σ is taken as implying permanent electron acceptance to hydrogen. Both Burawoy and

[41a] E. Berliner, M. C. Beckett, E. A. Blommers and B. Newman, *J. Amer. Chem. Soc.* **74**, 4940 (1952); [b] E. Berliner and L. H. Altschul, *Ibid.* **74**, 4110 (1952); [c] E. Berliner and L. C. Monack, *Ibid.* **74**, 1574 (1952).

[42] M. S. Newman and E. K. Easterbrook, *J. Amer. Chem. Soc.* **77**, 3763 (1955).

[43] C. W. L. Bevan, E. D. Hughes and C. K. Ingold, *Nature, Lond.* **171**, 301 (1953).

[44] This has been commented upon by Price and Lincoln, who attributed the smaller rate constant for the *p*-t-Bu compound in "56%" acetone to steric hindrance by the large *p*-alkyl group to solvation of the direct reaction site (i.e. the ester group) in the transition state; C. C. Price and D. C. Lincoln, *J. Amer. Chem. Soc.* **73**, 5836 (1951).

Schubert have questioned such a static viewpoint of substituent effects. They have presented evidence that certain substituents may function as either apparent electron donors or as apparent electron acceptors relative to hydrogen, at least in certain electronic transitions, and were led independently to a consideration of substituent effects in terms of the "polarizability" of the substituent. Burawoy and Thompson proposed that the apparent electron release by *p*-halogen substituents in electron demanding electronic transitions and the apparent electron acceptance by *p*-halogen substituents in electron donating electronic transitions is determined by the polarizability of the σ-electrons to the substituent.[45] Schubert and co-workers suggested that the extent of electron "release" or "acceptance" by a substituent in a given state can be considered to be a function of both the magnitude of the electronegativity difference between the substituent and the site to which it is bonded and what will here be labeled as "substituent-polarizability".[46] They applied this viewpoint to a consideration of the effect of *para* alkyl, halogen and other substituents on electron demanding transitions and to the effect of *p*-halogen substituents on electron donating transitions.[23,48] The substituent is viewed upon as being capable of being polarized with roughly equal ease in either a positive sense (electron "release" by the substituent) or a negative sense (electron "acceptance" by the substituent) depending on whether the site to which the substituent is attached is more or less electronegative than the substituent. The vague term "substituent-polarizability" skirts the question of the exact manner in which the substituent is polarized but is considered to include either or both direct polarization of the bonding electrons to the substituent (σ and also π-bonds, if any) and possible internal dispersion force polarization.[18,49]

According to the treatment of substituent effects in terms of "substituent-polarizability" and electronegativity, alkyl substituents would be expected to lower the energy of transitions in which a sufficiently strong migration of negative charge toward the substituent occurs. The authors therefore undertook to measure the effect of *p*-alkyl substituents on the energy and intensity of the principal electronic transitions of phenol, anisole, aniline, and N,N-dimethylaniline.[51] These transitions, in which the interaction with the electric vector of the light is in the long axis of the molecule,[52] can

[45] A. Burawoy and A. R. Thompson, *J. Chem. Soc.* 4314 (1956).

[46] This is equivalent to postulating that the energy, Δ, released in the hypothetical reaction, A:B (ideal covalent) → A-B (actual molecule), is empirically a function not only of the electronegativity difference between A and B but also of the ease with which interacting electrons between A and B are polarized, this depending on the nature of both A and B. Pauling, in setting up an empirical scale of electronegativities, assumed that Δ is a function of only the electronegativity difference, specifically that Δ = const. $(x_A - x_B)^2$; [47]

[47] L. Pauling, *The Nature of the Chemical Bond* Chap. II. Cornell University Press, New York, (1944).

[48a] W. M. Schubert, J. M. Craven, H. Steadly and J. Robins, *J. Org. Chem.* **22**, 1285 (1957); [b] W. M. Schubert, J. M. Craven and H. Steadly, *J. Amer. Chem. Soc.* **81**, 2695 (1959); [c] W. M. Schubert, H. Steadly and J. M. Craven, *Ibid.* **82**, 1353 (1960); [d]W. M. Schubert and J. M. Craven, *Ibid.* **82**, 1357 (1960).

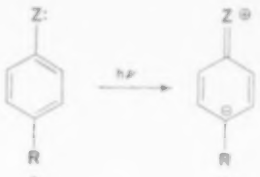
[49] The term "substituent-polarizability" is not to be confused with polarizability as determined from molar refractions. The "bond" or group refraction of a substituent is a measure of the ease with which the electrons are polarized by an external electro-magnetic field,[50] and thus is not necessarily a measure of the ability of the substituent to undergo internal polarization in an electronic transition. However, a parallelism between the two types of polarization may exist, as evidenced, e.g., by the correlation between the energies of the principal electronic transitions and the molar refractions of *p*-halo anisoles, nitrobenzenes and acetophenones.[48b]

[50] K. Fajans in Physical Methods of Organic Chemistry (Edited by A. Weissburger) Part II. p. 1163. Interscience, New York, (1949).

[51] Preliminary results were reported in reference 24.

[52] W. T. Simpson, *J. Amer. Chem. Soc.* **75**, 597 (1953); W. T. Simpson and C. W. Looney, *Ibid.* **76**, 6293 (1954).

be crudely represented by equation (1) (see e.g. refs. 52, 53).[54] That the electron migration in these transitions is indeed away from the functional group and toward the substituent is amply verified by the effects of solvents on the principal electronic transition energies of such compounds.[48d,53]



I II (1)

: Z = OH, OCH_3, NH_2, $N(CH_3)_2$

VOL. 17 1962

II. *Results*

Gas phase spectral measurements on carefully purified compounds were made in 20 cm Aminco quartz cells at elevated temperature with a Beckman DU instrument as previously described.[23,48] Measurements in heptane were made in 1 cm stoppered quartz cells at 25 ± 1°. Absorption maxima were located as previously described. Values of the transition moment length,[55] q, in heptane were calculated according to equation (2) from spectra measured in a Cary Model 14 instrument.

$$q^2 = 1{\cdot}09 \times 10^{-19} \int \epsilon \, \mathrm{d} \ln \lambda \qquad (2)$$

Representative of the principal band spectra of the members of each of the series are those of the *p*-methyl compounds in heptane, shown in Fig. 1. Each compound also exhibits a low intensity band ($\epsilon < 1000$) which has considerable fine structure and appears around 280 mμ. This evidently is the so-called B band, corresponding to the 260 mμ band of benzene. The principal band of the anilines and dimethylanilines is quite symmetrical, though overlapped slightly by a lower wave length band, and ν_{max} is probably a fairly accurate measure of the transition energy. The principal band of the phenols is considerably distorted through overlap by an intense lower wave length band. This is also true for the anisoles, but to a lesser extent. Thus, although the values of ν_{max} are precise to ±20–30 cm^{-1}, the limits of accuracy of ν_{max} for the phenols and the anisoles are probably much higher than this. Table 2 lists the ν_{max} values found in the gas phase. Table 3 lists values obtained in heptane of ν_{max}, ϵ_{max}, and q. For comparative purposes, values for *p*-alkylnitrobenzenes are included.

III. *Discussion*

p-*Alkyl vs.* p-*hydrogen.* Consider first the observation that *p*-alkyl substituents lower the principal electronic transition energy of phenol, anisole, aniline and dimethylaniline (Tables 2 and 3). The lower excitation energy for the *p*-alkyl compounds means that the quantity, $E_{II}^{\ddagger} - E_{R}^{\ddagger}$, is greater than the quantity $E_{II} - E_{R}$, where

[53] N. S. Bayliss and L. Hulme, *Aust. Chem. J.* **6**, 257 (1953); N. S. Bayliss and E. G. McRae, *J. Phys. Chem.* **58**, 1002 (1954); K. Bowden and E. A. Braude, *J. Chem. Soc.* 1068 (1952).

[54] Obviously the use of single valence bond depictions for ground and excited states is merely for convenience, and the depictions I and II are arbitrarily chosen as perhaps the single best *representative* structures. It is understood that polar structures such as II *may* also contribute to the ground state, but certainly not to the extent as to the excited state.

[55] G. S. Levinson, W. T. Simpson and W. Curtis, *J. Amer. Chem. Soc.* **79**, 4314 (1957); G. Herzberg, *Molecular Spectra and Molecular Structure* pp. 381–383. Van Nostrand, New York (1950).

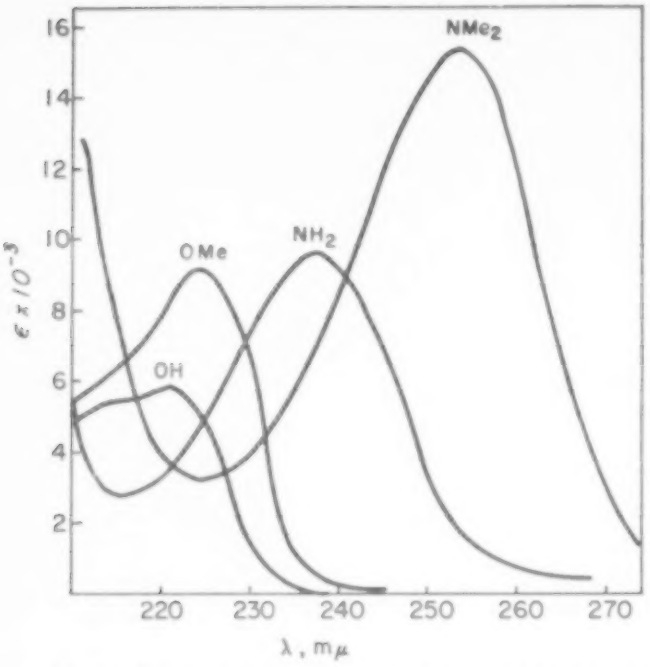


FIG. 1. Plot of the principal band spectra in heptane of the *p*-methyl derivatives of phenol, anisole, aniline and N,N-dimethylaniline.

TABLE 2. VALUES OF $\nu_{max.}$ (cm^{-1}) FOR p-RC_6H_4Z IN THE GAS PHASE[a]

Z	H	Me	t-Bu	NeoP
OH	48470[c]	46280[c]	46300[c]	45480
OCH_3[b]	46510	45500	45470	44880
NH_2	43590	42790	42970	42280
NMe_2	41360	(41070)[d]	(40900)[d]	—
NO_2[e]	41820	39970	39760	39490

[a] Average of three determinations at 150°, duplicable to ±20–30 cm^{-1}. A temperature of 150° was used to insure the absence of adsorption of the less volatile compounds on the cell windows.[23a]

[b] Also determined at 80°, with results within experimental error of those at 150°.

[c] Spectral peak highly unsymmetrical due to strong overlap by a lower wave length band.

[d] Of doubtful accuracy due to slow change of spectrum with time and temperature.

[e] Previously reported.[23a,b]

TABLE 3. VALUES OF ν_{max} (cm^{-1}), $\epsilon_{max} \times 10^{-3}$ AND TRANSITION MOMENT LENGTH, q(Å), FOR p-RC_6H_4Z AT 25° IN HEPTANE[a,b,c,d]

	H	Me	t-Bu	NeoP
Anisoles				
ν_{max}	45330	44750	44810	44270
$\epsilon \times 10^{-3}$	7·6	9·1	10·1	11·3
q[e]	0·50	0·56	0·62	0·64
Anilines				
ν_{max}	42740	42230	42320	41770
$\epsilon \times 10^{-3}$	9·0	9·5	10·7	11·6
q	0·66	0·69	0·74	0·77
N,N-Dimethylanilines				
ν_{max}	39830	39490	39600	—
$\epsilon \times 10^{-3}$	14·9	15·7	16·3	—
q	0·87	0·91	0·94	—
Phenols[f]				
ν_{max}	47430	45420	45500	44900
$\epsilon \times 10^{-3}$	5·7	5·9	6·8	8·0
q	—	—	—	0·55
Nitrobenzenes				
ν_{max}[g]	39700	37870	37670	37410
$\epsilon \times 10^{-3}$	8·7	10·0	11·0	11·7
q	0·80	0·86	0·90	0·95

[a] Values of ν_{max} are averages of three determinations, duplicable to ± 20 cm^{-1}.

[b] Values of ν_{max} also were determined for some of the compounds on the Cary Model 14 spectrophotometer. The differences in ν_{max} values obtained this way were within experimental error of those obtained on the Beckman DU.

[c] Values of $\epsilon_{max} \times 10^{-3}$ are averages of two determinations, duplicable to $\pm 2\%$.

[d] Values of q, equation (2), are averages of two determinations, duplicable to $\pm 1\%$, except where noted.

[e] Duplicable to $\pm 2\%$. Choice of area under principal band arbitrary due to overlap by lower wave length band.

[f] Except for the p-neopentyl derivative, the spectral band of the phenols was quite unsymmetrical due to strong overlap of the principal band by a lower wave length band. This prevented q from being accurately determined.

[g] Previously reported.[22a,b]

$E_H^{\ddagger}$ and $E_R^{\ddagger}$ are the energies of the excited states of the *p*-hydrogen and *p*-alkyl compounds, respectively; and E_H and E_R are the energies of the corresponding ground states. This implies that the excited state is *stabilized* through *p*-alkyl substitution, i.e. $E_H^{\ddagger} - E_R^{\ddagger}$ positive and $E_H - E_R$ less positive, zero, or negative; for if one assumes that the excited state is destabilized by *p*-alkyl substitution, i.e. $E_H^{\ddagger} - E_R^{\ddagger}$ negative, then one is forced to the unlikely conclusion that the much less polar ground state is destabilized even more by *p*-alkyl substitution, i.e. $E_H - E_R$ more negative than $E_H^{\ddagger} - E_R^{\ddagger}$. Since the electron migration in the principal electronic transitions of phenol, anisole, aniline and dimethylaniline is *away* from the functional group and *toward* the substituent, i.e. the excited state is electron rich in the region of the *p*-substituent, the results imply further that the *p*-alkyl substituents are functioning as apparent electron *acceptors* relative to the *p*-hydrogen substituent in the excited state of these transitions.[56]

The "activating" effect of *p*-alkyl substituents in the principal electronic transition of phenol, anisole, aniline and dimethylaniline is inconsistent with the current static viewpoint of the electronic effects of alkyl substituents, in which alkyl groups are considered as permanent electron donors relative to hydrogen and are pictured as resisting negative charge, e.g. by hyperconjugation (see e.g. refs. 41–43). A possible role of alkyl substituents as electron *acceptors* relative to hydrogen also seems nowhere to have received specific theoretical treatment, although Mulliken in a recent paper has written: "It seems to the writer that the customary use of a symbolism such as $H^{+}CH_2{-}CH{=}CH_2^{-}$ and corresponding emphasis on electron release, without any mention of an oppositely polarized ionic structure and, especially of the long bond structure $\overset{\frown}{H_3{-}C{-}CH{=}CH_2}$, may be seriously misleading".[8]

The flexible behavior of the *p*-alkyl substituents in functioning as apparent electron acceptors in the nucleophilic principal electronic transition of phenols, etc. and as apparent electron donors in electrophilic electronic transitions such as the principal electronic transition of nitrobenzene or acetophenone is qualitatively consistent with the treatment of substituent effects in terms of "substituent polarizability" and substituent electronegativity. This treatment can be graphically illustrated as in Fig. 2. The ordinate labeled *D*, the "demand for electrons", represents the electronegativity of A in the molecule A:X, where X is the substituent. Stabilization energy (positive) resulting from "electron release" by the substituent is given to the right on the *x*-axis. Stabilization energy (also positive) resulting from "electron acceptance" by the substituent is given to the left on the *x*-axis. The plot for two substituents of differing electronegativity and differing "substituent-polarizability", say H and CH_3, has been arbitrarily made linear. The origin of this plot is placed at the point of intersection of the *D*-axis with the line for the hydrogen substituent. At this value of *D* the hydrogen would neither release nor accept electrons, i.e. the electronegativity of A and H in A:H equal. For positive values of *D*, i.e. A in A:H more electronegative than H, H would "release" to A. For negative values of *D*, i.e. A less electronegative than H, H would "accept" from A. The slope of the arbitrary line is inversely related to the "substituent-polarizability".

[56] The term "apparent" electron acceptor is used here in recognition of the possibility that the stabilizing effect of the *p*-alkyl substituent on the excited state conceivably may be due at least in part to an internal dispersion force,[15] a type of interaction that does not involve a direct electron exchange between the substituent and the rest of the molecule.

The line for methyl has been given a smaller slope than that for hydrogen since methyl presumably has the greater "substituent-polarizability". In placing the intersection of the methyl line below the origin, the methyl substituent has been assumed to be less electronegative than the hydrogen substituent. This is in accord with the electronegativity order assigned by Walsh[57], Moffitt[58] and Bent[59]. It should be

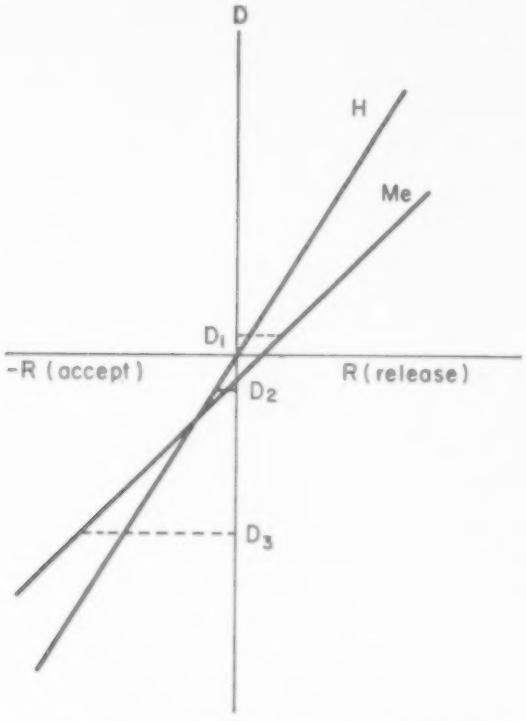


FIG. 2. Arbitrary electron demand–electron release plot for the H and CH_3 substituents. The *D* axis represents the electron demand placed on the substituent, X, by the varying group A in the ideal covalent molecule A:X. On the *x*-axis R represents positive stabilization energy resulting from electron release by the substituent and —R represents stabilization energy (also positive) resulting from electron acceptance by the substituent.

pointed out, however, that in the electronegativity tables of Pauling[47] and of Mulliken[60], tetrahedral carbon is assigned a greater electronegativity than hydrogen, and that this order has found more widespread use in the literature.

Consider now the principal electronic transitions of the phenols, etc. in terms of Fig. 2. In the ground state, the demand, *D*, placed on the *p*-substituent is neither very high nor very low. If, e.g. the demand is at D_1[61] the ground state would be stabilized through electron release in the order $CH_3 > H$. In the excited state the value of *D* is

[57] A. D. Walsh, *Proc. Roy. Soc.* A **207**, 13 (1951).
[58] W. Moffitt, *Proc. Roy. Soc.* A **207**, 74 (1951); *ibid.* A **202**, 534, 548 (1950).
[59] H. A. Bent, *J. Chem. Phys.* **32**, 1382 (1960).
[60] R. S. Mulliken, *J. Chem. Phys.* **2**, 782 (1934); *Ibid.* **3**, 573, 586 (1935).
[61] This is in accordance with an electronegativity order; $C^{sp^3} > H > C^{sp^3}$, for neutral atoms.[57,58]

probably quite low; i.e. the *p*-substituent is attached to a highly electron rich, electropositive center.[62] If D is sufficiently low, e.g. at D_3, the excited state of the *p*-methyl compound would be stabilized sufficiently over that of the *p*-hydrogen compound to insure a qualitative order of excitation energies $CH_3 < H$, even *if* the hydrogen substituent were more electronegative than the methyl substituent. Similarly, for the principal electronic transition of nitrobenzene or acetophenone, the very high D in the excited state (i.e. the *p*-substituent attached to a highly electron deficient, electronegative center)[62] would also insure an excitation energy order $CH_3 < H$, even if the hydrogen substituent were less electronegative than the methyl substituent.

With this treatment one could also rationalize why a *p*-alkyl substituent is "deactivating" in ordinary nucleophilic chemical transitions although "activating" in the nucleophilic electronic transitions, *provided* the hydrogen substituent is indeeed more electronegative than the alkyl substituent. In other words, a higher D value (i.e. smaller electron deficiency at the *p*-position in the transition state of the nucleophilic chemical transition as compared to the nucleophilic electronic transitions)[62] could result in the order, $H < CH_3$, for the activation energies. For example, if D in the transition state is only at D_2 the transition state would be stabilized in the electronegativity order. If D in the transition state is below the intersection of the hydrogen and methyl lines, the transition state would be stabilized in the substituent polarizability order. However, unless D is sufficiently low, the transition state would be stabilized less by the *p*-methyl relative to the *p*-hydrogen substituent than the ground state (ground state D say at D_1) and the activation energies would still be in the electronegativity order.[64] A greater electronegativity for the hydrogen than the alkyl substituent would also be consistent with the fact that alkyl substituents are activating even in mildly electrophilic transitions.

Effect of changing p-*alkyl substituent.* The energy order for the nucleophilic electronic transitions is neoP $< CH_3$, t-Bu $<$ H, with the *p*-methyl and *p*-t-butyl groups having comparable effects. In heptane (Table 3), the ν_{max} values of the *p*-methly and *p*-t-butyl compounds lie within experimental error of each other in the phenol and anisole series and in the order $CH_3 <$ t-Bu in the aniline and N,N-dimethylaniline series. In the gas phase (Table 2) the *p*-methyl-*p*-t-butyl ν_{max} order is clearly established only in the aniline series, it also being $CH_3 <$ t-Bu.

[62] Application of the Hammett equation,[59,60] $\log k_X - \log k_H = \frac{1}{2{\cdot}3RT}(\Delta F_H^{\ddagger} - \Delta F_X^{\ddagger}) = \sigma_X\rho$, to the principal electronic transition of nitrobenzene substituted in the *p*-position with substituents, X, having a negative substituent constant, σ_X, gives a ρ value for this reaction of $-13{\cdot}0 \pm 1{\cdot}2$. Preliminary estimates of the ρ values for the nucleophilic principal electronic transitions of *p*-substituted phenols, anisoles and anilines are 14·5, 9·8, and 7·0 respectively.[63] Applying the criterion that the magnitude of the ρ values is a measure of the nucleophilic demand placed on the substituent, it is clear that the *p*-substituent is called upon much more strongly to "accept" electrons in the principal electronic transitions of phenol, etc., than in the chemical reactions of Table 1. A large increase in polarity in the excited state is also reflected in the large degree to which the excitation energy is lowered in heptane relative to the gas phase (of the order of 3 kcal/mole), despite the unfavorable partial orientation of the solvent to the Franck–Condon excited state.[45c] The large negative ρ values for the principal electronic transition of nitrobenzenes and acetophenones also have a much greater magnitude than the ρ values found for electrophilic chemical transitions and are indicative of a stronger electron demand on the substituent.

[63] James M. Craven, Ph.D. Thesis, University of Washington (1959).

[64] Those who have maintained that alkyl groups function as permanent electron donors relative to hydrogen in nucleophilic reaction generally have neglected to consider the ground states;[61–63] i.e. they have failed to take cognizance of the possibility that the (presumably) greater activation energy for the *p*-alkyl compounds could be the qualitative result of the greater ground state stability of the alkyl compound.

The energy order in electrophilic principal electronic transitions is neoP < t-Bu < CH_3 < H (see Tables 2 and 3 for the previously determined ν_{max} values for the nitrobenzenes). Thus, except for an inversion of the methyl-t-butyl order in some instances, the effect of *p*-alkyl substituents on the energies of the nucleophilic electronic transitions are qualitatively the same as their effect on the energies of the electrophilic electronic transitions. The qualitatively comparable effects of the *p*-alkyl substituents in the two types of transitions is consistent with the naive consideration of substituent effects in terms of "substituent-polarizability" and electronegativity, and indeed, the instances of the inversion of the methyl-t-butyl order could be rationalized in terms of a slightly greater electronegativity for the *p*-methyl substituent coupled with a slightly greater "substituent-polarizability" for the *p*-t-butyl substituent.[65] The values in heptane of the transition moment length *q*, a quantity determined from the area of the absorption band (equation 2) and considered to measure the extent of *oscillation* of the solute dipole *during* the interaction with the electric vector of the light being absorbed[55] take exactly the same order for the nucleophilic electronic transitions as for the electrophilic excitation of nitrobenzene (Table 3). The order of *q* is neoP > t-Bu > CH_3 > H, and is considered to correspond to the order of "substituent-polarizability".

It is a matter of conjecture as to just what specific mechanisms are operative in the stabilization by *p*-alkyl substituents of the attached electron rich site in the excited state of phenol, etc. One question that can be asked is whether substituent polarization occurs through space (internal dispersion force)[18] or the bonding electrons, or whether both modes of polarization are important. Polarization of the bonding electrons to the substituent *might* include hyperconjugative electron acceptance[66] (both C—H and C—C) in addition to including inductomeric electron acceptance (i.e. polarization of the σ-bonding electrons between the substituent and the ring).

The fact that the *p*-neopentyl substituent lowers the excitation energy, and increases the transition moment length, of both nucleophilic and electrophilic electronic transitions to a greater extent than either the *p*-methyl or *p*-t-butyl substituent is difficult to explain solely in terms of either an inductomeric or hyperconjugative effect, or both. An internal dispersion force interaction may be of importance in the total effect of the neopentyl substituent. In molecular models a terminal portion of the *p*-neopentyl group is held in close juxtaposition to one side of the aromatic ring in the neighborhood of the *p*-position, in a particularly favorable position for polarization through space. That is, the terminal portion of the neopentyl group "may be acting in much the same way as would an adhering hydrocarbon solvent molecule",[23b] thus helping to stabilize either an electron rich or electron deficient aromatic ring in the excited state.

The neopentyl group also appears to be exerting an exceptional stabilizing effect on the ground state of ethylene. Whereas the heats of hydrogenation of propylene, 1-butene, isopropylethylene and t-butylethylene are identical within experimental error (the values are −30·1, −30·3, −30·3, and −30·3 kcal/mole, respectively, compared with −32·8 for ethylene), the heat of hydrogenation of neopentylethylene is significantly greater (−29·5 kcal/mole).[33]

[65] *If* CH_3 is less electronegative than H, then the t-Bu group (having three α-methyl groups) probably should be less electronegative than the CH_3 group (having three α-hydrogens).

[66] Hyperconjugative electron acceptance could be labeled "anionoid" hyperconjugation; see, e.g. F. H. Siebold, Jr., *J. Org. Chem.* **21**, 156 (1956), for the use of this term.

Effect of changing functional group. In Tables 2 and 3 it is seen that for the parent compounds of each series, or for the derivatives substituted with any particular *p*-alkyl substituent, the excitation energies decrease and the transition moment lengths increase in the order OH, OCH_3, NH_2, $N(CH_3)_2$. The functional group effect is rather large. For example, the difference in excitation energy between phenol and N,N-dimethylaniline in the gas phase is 7110 cm^{-1}, or 20·3 kcal/mole. Accompanying a decrease in excitation energy with functional group change is a decrease in the excitation energy spread between the *p*-hydrogen and the *p*-alkyl derivatives. For example, $\nu_H - \nu_{CH_3}$ in heptane has the value 2010 cm^{-1} (5·8 kcal/mole) for the phenols and decreases to only 340 cm^{-1} (1·0 kcal/mole) for the N,N-dimethylanilines. A similar parallelism between decreasing excitation energy of the parent compound and a decreased sensitivity of the excitation energy to the *p*-substituent has been noted previously for *p*-halo phenols, anisoles and anilines, and is reflected in the order of the Hammett "reaction" constants, ρ.[62]

Acknowledgements—The authors wish to thank the Office of Ordnance Research, United States Army, for partial financial support of this research. The hospitality extended to one of us (W. M. S.) by Prof. Th. Förster of the Laboratorium für Physikalische Chemie und Elektrochemie der Technischen Hochschule, Stuttgart, Germany, also is gratefully acknowledged.

Tetrahedron, 1962, Vol. 17, pp. 215 to 228. Pergamon Press, Ltd. Printed in Northern Ireland

VOL. 17 1962

BOND LENGTHS IN CYCLIC POLYENES $C_{2n}H_{2n}$ A RE-EXAMINATION FROM THE VALENCE-BOND POINT OF VIEW

C. A. COULSON and W. T. DIXON
Mathematical Institute, Oxford

(*Received* 16 *February* 1961)

Abstract—The valence-bond resonance method for predicting bond lengths in conjugated hydrocarbon molecules has been reconsidered. New values are obtained for the variation of the fundamental exchange and Coulomb integrals with bond length. Application to the cyclic polyenes $C_{2n}H_{2n}$ shows that for large n there will be substantial bond alternation. Inclusion of Dewar structures diminishes this alternation, but does not destroy it.

1. INTRODUCTION

TWENTY-TWO years ago Lloyd and Penney[1] made calculations of the bond lengths in certain small conjugated molecules (e.g. butadiene and benzene) using the valence-bond (v.b.) method of resonance. But since that time practically no further calculations have been made with this approximation, and the molecular-orbital (m.o.) method has been almost exclusively adopted. During the last few years, however, several new considerations have been proposed, leading to substantial changes in our opinion with regard to several matters previously regarded as settled. Thus (1) the influence of the compressional energy[2–5] is now recognised to be of supreme importance in determining equilibrium bond lengths; (2) in any use of an order–length relationship to link bond order with bond length, it is admitted that the covalent radius of a trigonal carbon atom is less than that of a tetrahedral carbon atom, thus leading to a displaced order–length curve, in which the C—C single bond length[6,7] is about 1·50–1·51 Å; (3) in long chain polyenes $C_{2n}H_{2n+2}$ and in large cyclic polyenes $C_{2n}H_{2n}$ the bonds do not tend to equality[8] as n increases, but rather there is an alternating character represented, in an exaggerated form, by the familiar bond diagram = — = — = . . . = — =. The situation of equal lengths, as originally predicted[9] by naive use of simple bond order calculations, turns out to be a saddle point and not a true minimum of the energy. For large molecules the alternation of bond length is of

[1] E. H. Lloyd and W. G. Penney, *Trans. Faraday Soc.* **35**, 835 (1939).
[2] J. E. Lennard-Jones, *Proc. Roy. Soc.* A **158**, 280 (1937).
[3] R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Amer. Chem. Soc.* **63**, 41 (1941).
[4] C. A. Coulson, *Victor Henri Memorial Volume* p. 15. Desoer, Liège (1948).
[5] C. A. Coulson and S. L. Altmann, *Trans. Faraday Soc.* **48**, 293 (1952).
[6] H. J. Bernstein, *J. Phys. Chem.* **63**, 565 (1959).
[7] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959) who suggest an even shorter value 1·48 Å.
[8] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* A **251**, 172 (1959) and later papers by the same authors.
[9] C. A. Coulson, *Proc. Roy. Soc.* A **169**, 413 (1939).

the order of 0·04 Å. A similar alternation is also predicted[10]—though with rather larger disparity between the shorter and longer bonds, of the order of magnitude 0·09 Å—in the hypothetic bridged ring molecule pentalene C_8H_6 (see I).

I

The results in references 8 and 10 were all obtained using the m.o. method, though without configuration interaction. It would seem desirable, therefore, to see to what extent the predictions depend on using this method. We have therefore thought it worthwhile to re-examine the same problems within the v.b. approximation. For this purpose it would have been pleasant to be able to use the numerical values of exchange and Coulomb integrals obtained by Lloyd and Penney[1], but we have not done so, and have preferred to work independently, though in a very similar spirit. In the first place the calculations of Lloyd and Penney require to be corrected so as to take account of the revised C—C trigonal single-bond radius, referred to in (2) above; and in the second place Lloyd and Penney, in their anxiety to take full account of all exchange terms, appear to us (see also reference 5 where further comments are made on this work) to have taken a σ-π exchange integral equal in magnitude to π-π exchange integrals. A rough estimation of these integrals suggests that this is not very probable, and so also does an elementary consideration of the likely contributions to the exchange integral from different regions of space. When we allow for these two changes, somewhat different curves are obtained for the Coulomb integral $Q(r)$ and the exchange integral $J(r)$ as functions of the bond length r.

The first part of this paper is therefore concerned with using certain experimental molecular magnitudes to deduce empirical $Q(r)$ and $J(r)$ curves. In the second part we show that when proper allowance is made for the σ-bond compressional energy, cyclic polyenes $C_{2n}H_{2n}$ are not expected to be regular polygons except for small n (in complete agreement with the m.o. results) though the critical value of n at which alternation sets in cannot yet be predicted accurately, since the Dewar-structures and more highly-excited structures also serve partly to weaken the strong tendency of the Kekulé structures to induce bond alternation. This surprising result differs from the usual belief that resonance among Kekulé structures tends to cause equality of bonds: but a very simple calculation does in fact show that this is not necessarily the case. Finally we present some detailed calculations for the cyclic polyenes $C_{2n}H_{2n}$ in which $2n = 6, 8$ and 10. Except in the case of benzene ($2n = 6$) these calculations are only illustrative, since neither C_8H_8 nor $C_{10}H_{10}$ are planar molecules. But we believe that these calculations, all made on the assumption of planarity, are sufficient to illustrate the general conclusions obtained earlier. We have also tacitly assumed all the valence angles to be 120°. Apart from benzene, this is manifestly impossible geometrically for small values of n. But it is possible, and probably occurs, for the larger molecules which have been isolated experimentally, and which we shall discuss in Sections 3 and 4.

[10] P. C. den Boer-Veenendaal and D. H. W. den Boer, *Molec. Phys.* **4**, 33 (1961).

2. THE FUNCTIONS $Q(r)$ AND $J(r)$

Let us represent the total energy of a π-electron molecule in the form

$$E_{\text{total}}(r_1, \ldots) = E_\sigma(r_1, \ldots) + E_\pi(r_1, \ldots) + E_{\pi\sigma}(r_1, \ldots) \tag{1}$$

where

$r_1, \ldots$ are the various bond lengths
E_σ is the total σ-bond energy
E_π is the total π-electron energy
$E_{\pi\sigma}$ is the total π-σ exchange energy.

We shall now make the assumption that either $E_{\pi\sigma}$ is so small in relation to the other terms of (1) that it may be neglected, or else it varies with bond lengths in so similar a way to E_σ that it may be incorporated in this latter function. This seems very reasonable, at least for molecules such as those being considered in this paper, for the distributions of π and of σ electrons are effectively uniform. It might, however, be less valid if heteroatoms were present, such as in pyridine. Thus (1) is replaced by

$$E_{\text{total}}(r_1, \ldots) = E_\sigma(r_1, \ldots) + E_\pi(r_1, \ldots) \tag{2}$$

In order to use this formula to determine the Coulomb and exchange integrals $Q(r)$ and $J(r)$ we must choose two molecules for which E_{total} is known experimentally; and we must also know the corresponding expressions for E_π and E_σ. If we adopt the usual approximations of orthogonality of all atomic orbitals, then the method of Pauling[11] enables us to write for ethylene

$$E_\pi^{\text{ethylene}}(r) = Q(r) + J(r), \tag{3}$$

and for benzene, when all bonds are equal

$$E_\pi^{\text{benzene}}(r) = 6\{Q(r) + 0{\cdot}434\, J(r)\} \tag{4}$$

In writing (3) and (4) we have made the usual assumption that $Q(r)$ and $J(r)$ are the same functions of r for benzene and for ethylene. This implies—at very least—that we neglect direct *meta*- and *para*-interactions in the benzene ring. If we consider the two molecules at the same bond distance r, then $E_\sigma^{\text{benzene}}(r) = 6E_\sigma^{\text{ethylene}}(r)$, and so, using (3) and (4)

$$E_{\text{total}}^{\text{ethylene}}(r) - \tfrac{1}{6}E_{\text{total}}^{\text{benzene}}(r) = 0{\cdot}566\, J(r) \tag{5}$$

Empirical curves of $E_{\text{total}}(r)$ for ethylene and $\frac{1}{6}E_{\text{total}}(r)$ for benzene are drawn in Fig. 1. According to (5) their difference enables us to draw the curve of the exchange integral $J(r)$. This is also shown in the figure.

In drawing the curves for $E_{\text{total}}(r)$ we have used Morse functions of the usual form

$$W(r) = W_0\{e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}\} \tag{6}$$

where the values adopted (which, apart from r_0, are identical with those adopted by Lloyd and Penney) are as shown in Table 1. Any alteration in the latent heat of sublimation of carbon would affect the values of W. For purposes of comparison we have accepted for our own calculations precisely the same values as Lloyd and Penney. These differ very little from the best modern values, and in such a way as to make only very minute changes in the calculated bond lengths. The values of r_0 in this table are

[11] L. Pauling, *J. Chem. Phys.* **1**, 280 (1933). For a simple account see C. A. Coulson, *Valence* pp. 228–236. Oxford University Press (1952).

now firmly established, and the parameter (a) is dependent upon the fundamental breathing frequency of each molecule. It is worth reporting that in some preliminary calculations we had tried to avoid the complication of a Morse function, with its exponential terms, by using a harmonic oscillator expression $\frac{1}{2}k(r - r_0)^2$ for the energy

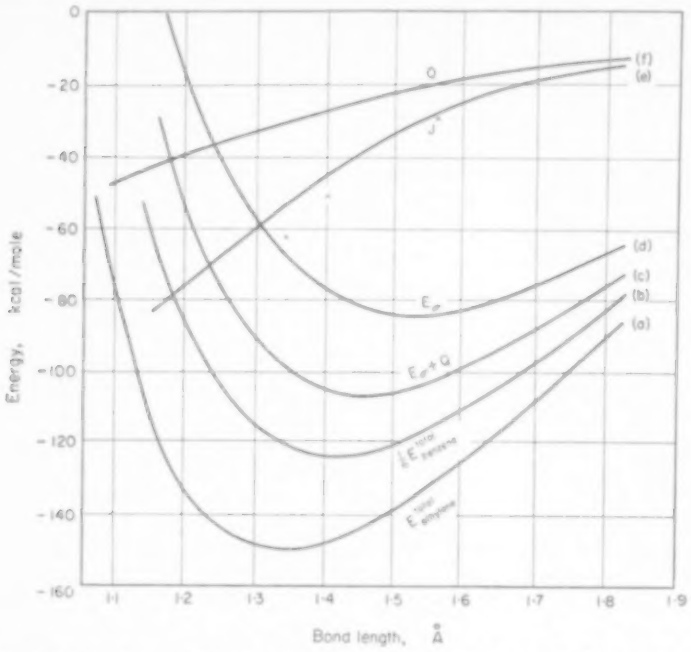


FIG. 1. (a) total energy E_{total} for ethylene (experimental); (b) one-sixth of total energy E_{total} for benzene (experimental); (c) $E_\sigma(r) + Q(r)$ deduced from (a) and (b); (d) assumed form of $E_\sigma(r)$; (e) $J(r)$ deduced from (a) and (b); (f) $Q(r)$ deduced from (c) and (d); crosses denote values of $J(r)$ calculated by Altmann[12].

TABLE 1

	W_0 (kcal/mole)	a (Å^{-1})	r_0 (Å)
Ethylene	151	2·189	1·34
Benzene	124	2·093	1·40
Ethane	84	2·028	1·54

of a σ-bond. This expression is the one most widely used in m.o. calculations. But we found that the resulting $J(r)$ curve was seriously affected by this, and its use gave absurd numerical results for the equilibrium bond lengths of cyclic molecules. We therefore abandoned it, with regret. As an indication of the serious dependence of $J(r)$ on the choice of a Morse function of $E_{\text{total}}(r)$ instead of a parabolic law, we show in Fig. 2 rough diagrams of $J(r)$ and $Q(r)$ obtained by both techniques. It will be noticed at once that the curvature of $J(r)$ is changed in sign. This implies that d^2J/dr^2 also changes sign. Now questions of stability of a given set of bond lengths depend on the sign of d^2E_{total}/dr^2. Thus, if $J(r)$ plays any significant part in fixing the equilibrium

[12] S. L. Altmann, *Proc. Roy. Soc.* A **210**, 327, 343 (1951).

bond length—as it most clearly does—we can see why we may be led to unacceptable positions of stability or instability, if we abandon Morse functions in favour of the simpler parabolic ones. All our later work, therefore, will use only the Morse functions (6) and the parameters of Table 1.

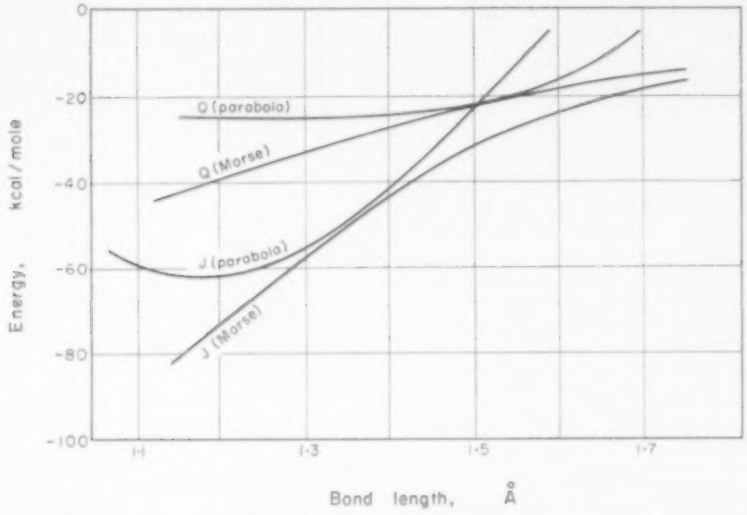


FIG. 2. Curves showing difference between exchange integral $J(r)$ and Coulomb integral $Q(r)$ with use of parabolic or Morse potential functions for ethylene and benzene.

We have still to determine $Q(r)$ and $E_\sigma(r)$ where this latter quantity is the σ-bond energy for a bond of length r, so that

$$E_\sigma(r_1, r_2 \ldots) = E_\sigma(r_1) + E_\sigma(r_2) + \ldots \tag{7}$$

Equations (2), (3), (4) and (7) allow us to write

$$E_\sigma(r) + Q(r) = 1{\cdot}767\,\frac{E_{\text{total}}^{\text{benzene}}(r)}{6} - 0{\cdot}767 E_{\text{total}}^{\text{ethylene}}(r) \tag{8}$$

We have shown this quantity in Fig. 1. Since it depends only upon equations (2), (3), (4) and (6) it is independent of any assumptions that we may make about the nature of $E_\sigma(r)$, other than that the π-σ interactions are included in it.

Table 2, columns 2 and 3, shows the values of $J(r)$ and $E_\sigma(r) + Q(r)$, both in kcal/mole for various values of r, in Å. This is the table of values which we shall use in our later numerical work. At this stage it is not necessary to separate $E_\sigma(r)$ and $Q(r)$, since in all our applications we shall find that it is their sum which appears. This would not be the case if we were considering heteronuclear molecules, and then we should find that each was required separately. Simple analytical approximations to the functions in Table 2—valid to within 0·020 kcal. in the range $1{\cdot}34 < r < 1{\cdot}51$—are

$$J(r) = -41{\cdot}199 + 121{\cdot}2(r - 1{\cdot}42) - 114{\cdot}2(r - 1{\cdot}14)^2 \tag{9}$$

$$E_\sigma(r) + Q(r) = -105{\cdot}905 - 39{\cdot}6(r - 1{\cdot}42) + 526(r - 1{\cdot}42)^2 - 1000(r - 1{\cdot}34)(r - 1{\cdot}42)(r - 1{\cdot}51) \tag{10}$$

The last figure in these numerical values is entirely without significance in any absolute sense: but for locating stationary values of the total energy it may have some significance.

There is not very much with which we may compare the numerical entries in Table 2. But Altmann[12], in some studies of the ethylene molecule, calculated $J(r)$,

TABLE 2

	Kekulé and Dewar structures		Kekulé structures only	
r	$-J(r)$	$-[E_\sigma(r) + Q(r)]$	$-J(r)$	$-[E_\sigma(r) + Q(r)]$
1·34	51·625	99·375	48·70	102·30
1·36	48·892	101·834	—	—
1·37	47·557	102·839	44·86	105·54
1·38	46·236	103·707	—	—
1·39	44·927	104·449	—	—
1·40	43·650	105·056	41·18	107·53
1·41	42·411	105·539	40·01	107·94
1·42	41·199	105·905	38·83	108·27
1·43	39·992	106·183	—	—
1·44	38·790	106·371	36·59	108·57
1·45	37·653	106·432	—	—
1·48	34·336	106·148	32·39	108·09
1·51	31·206	105·211	29·44	106·98

using a full twelve-electron Hamiltonian. For the distances 1·34, 1·39 and 1·54 Å he found values −62·9, −52·4 and −28·6 kcal respectively. These vary in the right way as our values, and are of the right order of magnitude, though they differ by about 10 kcal for short bonds. In view of the different types of approximation involved in the two estimates of $J(r)$, this is probably as good agreement as may be expected.

If we wish to go further than this, and obtain expressions for $E_\sigma(r)$ and $Q(r)$ separately, we must use some additional data. The most natural is $E_\sigma(r)$, which we could approximate as if it were the energy of a single bond between two trigonal carbon atoms. For this purpose we use a Morse curve in which the equilibrium length is not 1·54 Å, as in ethane, but is taken to be 1·51 Å, to allow for point (2) in the Introduction. It is not quite obvious which values we should choose for W_0 and a in equation (6); but we have, somewhat arbitrarily, chosen −84 kcal/mole and 2·028 Å^{-1} respectively. With this choice we can draw the $E_\sigma(r)$ curve of Fig. 1, and so determine $Q(r)$. For obvious reasons this curve is much less reliable than $E_\sigma(r) + Q(r)$, but in the region $1{\cdot}34 < r < 1{\cdot}54$ Å, it may be represented approximately by

$$Q(r) = -25{\cdot}275 + 49{\cdot}9(r - 1{\cdot}42) - 53{\cdot}5(r - 1{\cdot}42)^2 \qquad (11)$$

The difference between (10) and (11) is, of course, a representation of $E_\sigma(r)$.

We have now obtained approximate values of $J(r)$, $Q(r)$ and $E_\sigma(r)$. These are ready for application to our cyclic molecules. But before proceeding there is a point to consider. In (4) we have used the energy expression for the π-electrons of benzene, taking into account Kekulé and Dewar structures. It is not immediately obvious that we have any right to use this formula—and the implied $J(r)$—in larger molecules, where there will also be doubly-excited and more highly excited structures. But we shall assume that this is so, and shall try, when dealing with other molecules, to write

down the expression for E_π analogous to (4), neglecting all structures other than the Kekulé and first-excited ones. It is doubtful that inclusion of the more highly-excited structures would seriously affect the predicted bond lengths and stabilities, though it is known[13] that for sufficiently large conjugated molecules the more highly-excited

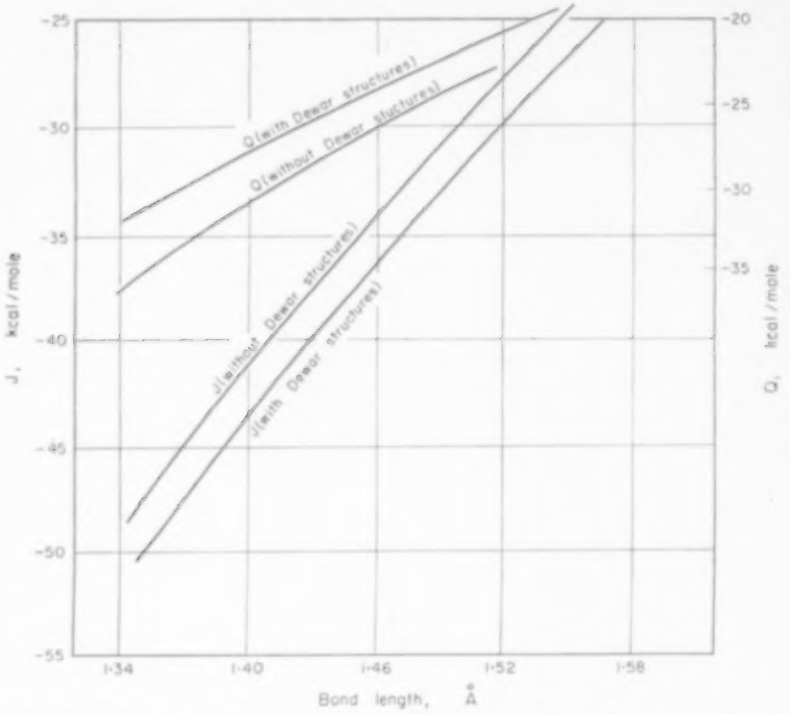


FIG. 3. Curves showing variation of exchange integral $J(r)$ and Coulomb integral $Q(r)$ when Dewar structures are included and when they are not included.

structures dominate over the less-excited. However, we can make an alternative calculation, in which we consider only Kekulé structures. If we do this, equation (3) is unchanged, and equation (4) is replaced by

$$E_\pi^{\text{benzene}}(r) = 6\{Q(r) + 0{\cdot}400\,J(r)\} \tag{12}$$

By an entirely similar process, this leads to values of $J(r)$ and $Q(r)$ which differ slightly from those previously determined (Table 2, columns 4 and 5). Fig. 3 shows, on a larger scale than Fig. 1, the variation of $J(r)$ and $Q(r)$ both with and also without inclusion of Dewar structures in benzene. The general variations are remarkably similar, leading to the view that predictions based on them would also be similar. Table 2 also allows a direct comparison of the values of $J(r)$ and $E_\pi(r) + Q(r)$ in these two approximations.

3. THE CYCLIC POLYENES $C_{2n}H_{2n}$, n LARGE

Consider the cyclic polyene $C_{2n}H_{2n}$, represented for the case of $n = 4$, by II. We are supposing that the molecule is planar. This is known not to be true for cyclo-octatetraene (II), but it must be more nearly true for the larger systems $2n = 18$, 24

[13] See C. A. Coulson, *Proc. Roy. Soc.* A **207**, 91 (1951).

and 30 synthesized by Sondheimer, Wolovsky and Gaoni[14,15,16]. Let us suppose also, for the moment, that we use only the Kekulé structures. There are just two of these, for all n, and they are represented by (a) and (b). We have allowed for possible bond alternation by letting the bond lengths be alternately r_1 and r_2. If $r_1 < r_2$, as in the

(a) (b)

II

diagram, the structure (a) will be more energetically bonding than (b), and, as Coulson and Altmann[5] showed for the case of benzene ($2n = 6$), the resonance energy is drastically reduced as $r_2 - r_1$ increases. Thus when $r_1 = r_2 = 1{\cdot}39$ Å they found that the delocalization energy, defined as the difference in E_π between the localized bonding of a Kekulé structure and the delocalized energy of the corresponding resonance hybrid, was about 63 kcal/mole. But when $r_1 = 1{\cdot}39$ Å, $r_2 = 1{\cdot}54$ Å (they used the old value for the length of a pure trigonal carbon–carbon bond), the delocalization energy was only 9·6 kcal/mole. We shall now show that even when 2n is large, resonance of this kind contributes relatively little to the delocalization energy, and is certainly insufficient to favour a regular shape with equal bond lengths.

If we write ψ_a and ψ_b for the Kekulé structures, and if the ground state wave function is

$$\Psi = c_1\psi_a + c_2\psi_b,$$

then the secular equations to determine the π-electrons energy E_π and the coefficients c_1, c_2 take the form

$$\begin{aligned}
&(nQ_1 + nQ_2 + nJ_1 - \frac{n}{2}J_2 - E_\pi)c_1 + \frac{1}{2^{n-1}}(nQ_1 + nQ_2 + nJ_1 + nJ_2 - E_\pi)c_2 = 0 \\
&\frac{1}{2^{n-1}}(nQ_1 + nQ_2 + nJ_1 + nJ_2 - E_\pi)c_1 + (nQ_1 + nQ_2 + nJ_2 - \frac{n}{2}J_1 - E_\pi)c_2 = 0
\end{aligned} \tag{13}$$

In these equations Q_1 and Q_2 are the two Coulomb integrals, appropriate to bond lengths r_1 and r_2, and J_1, J_2 are the corresponding exchange integrals. The interesting feature of these equations lies in the coefficient $1/2^{n-1}$ multiplying the off-diagonal elements in the resulting secular determinant. In the case of benzene this factor is 1/4, but for larger molecules it rapidly decreases, so that the roots of the secular determinant are given essentially by the diagonal elements. In fact, if $r_1 < r_2$ the lowest root is approximately

$$E_\pi = n\left[Q_1 + Q_2 + J_1 - \tfrac{1}{2}J_2 + \frac{3J_2^2}{2^{2n-1}(J_1 - J_2)}\right] \tag{14}$$

Thus the delocalization energy, which is given by the last term in (14) actually tends

[14] F. Sondheimer and R. Wolovsky, *Tetrahedron Letters* No. 3, 3 (1959).
[15] F. Sondheimer and R. Wolovsky, *J. Amer. Chem. Soc.* **81**, 4755 (1959).
[16] F. Sondheimer, R. Wolovsky and Y. Gaoni, *J. Amer. Chem. Soc.* **82**, 755 (1960).

to zero as $n \to \infty$. In the case where $J_1 = J_2$ the approximation (14) must be replaced by:

$$E_\pi = n\left[2Q + \frac{J}{2}\left(\frac{1 + (1/2^{n-3})}{1 + (1/2^{n-1})}\right)\right] \tag{15}$$

Here again it follows that for sufficiently large n, the delocalization energy tends to zero.

Thus on the basis of Kekulé structures alone, the larger cyclic polyenes would not be expected to be as stable as the smaller ones.

But we can also show that for sufficiently large n, the regular polygon with $r_1 = r_2$ is less stable than the alternating one with (say) $r_1 < r_2$. To do this we consider $E_{\text{total}}(r_1,r_2)$, which is the sum of E_π and E_σ where $E_\pi(r_1r_2)$ can be found from the equations (13), and where $E_\sigma(r_1r_2) = nE_\sigma(r_1) + nE_\sigma(r_2)$. It is obvious from symmetry considerations alone that there is a stationary value of the total energy when $r_1 = r_2$ and their common value is such that

$$\frac{d}{dr}\left[E_\sigma(r) + Q(r) + \frac{1}{4}\left(\frac{1 + (1/2^{n-3})}{1 + (1/2^{n-1})}\right)J(r)\right] = 0 \tag{16}$$

This common value differs very little from that appropriate to benzene, though it actually increases slowly with n. With $r = 1{\cdot}400$ for $n = 3$, it becomes $1{\cdot}403$ for $n = 4$ and $1{\cdot}413$ for $n = 5$.

A tedious calculation, which we shall not reproduce, but which uses the appropriate $J(r)$ and $Q(r)$ from Fig. 3, shows that, at these stationary values, E_{total} is an absolute minimum in the case of benzene, but a saddle point for $n = 4$ and $n = 5$ and all higher values of n. Thus, using Kekulé structures only, benzene is predicted to be a regular polygon, but all larger even cyclic molecules should show bond alternation.

It is not possible to give a similar general demonstration when Dewar structures are included in addition to the Kekulé structures. But (see later) detailed calculation of the energy contours for a variety of values of r_1 and r_2 shows that almost certainly precisely the same situation obtains. We conclude, therefore, that in the larger cyclic polyenes the configuration of greatest stability is one with alternating bond lengths, in agreement with the results of m.o. theory.[8] But in our v.b. theory the alternation appears to set in earlier than in the m.o. theory. In view of the approximations in both, such divergencies are not altogether surprising.

It is worth writing down the expression for the total energy, which results from solving equations (13) for E_π and then adding E_σ. It will be convenient to write $\mathscr{E}_1$ for $E_\sigma(r_1) + Q(r_1)$, and $\mathscr{E}_2$ for $E_\sigma(r_2) + Q(r_2)$. Then for benzene, where $2n = 6$, and taking the negative value of the square root,

$$E_{\text{total}}(r_1,r_2) = 3\mathscr{E}_1 + 3\mathscr{E}_2 + \tfrac{3}{2}(J_1 + J_2) + \tfrac{3}{2}\{4(J_1 - J_2)^2 + J_1J_2\}^{\frac{1}{2}}$$

for the case where $2n = 8$,

$$E_{\text{total}}(r_1,r_2) = 4\mathscr{E}_1 + 4\mathscr{E}_2 + \tfrac{8}{11}(J_1 + J_2) + \tfrac{16}{11}\{16(J_1 - J_2)^2 + J_1J_2\}^{\frac{1}{2}}.$$

For the case where $2n = 10$,

$$E_{\text{total}}(r_1,r_2) = 5\mathscr{E}_1 + 5\mathscr{E}_2 + \tfrac{25}{17}(J_1 + J_2) + \tfrac{5}{17}\{64(J_1 - J_2)^2 + J_1J_2\}^{\frac{1}{2}}.$$

Once again we see the growing importance of $J_1 - J_2$ as the size of the polyene increases.

4. DETAILED CALCULATIONS FOR 2n = 6, 8, 10

In more detailed calculations for the smaller molecules of this type, we have included both Dewar and Kekulé structures. In the case of benzene, with $r_1 \neq r_2$ there are five structures. The two Kekulé structures III(a)(b) will have different weights but the three Dewar structures, of which III(c) is one example, will all have the same

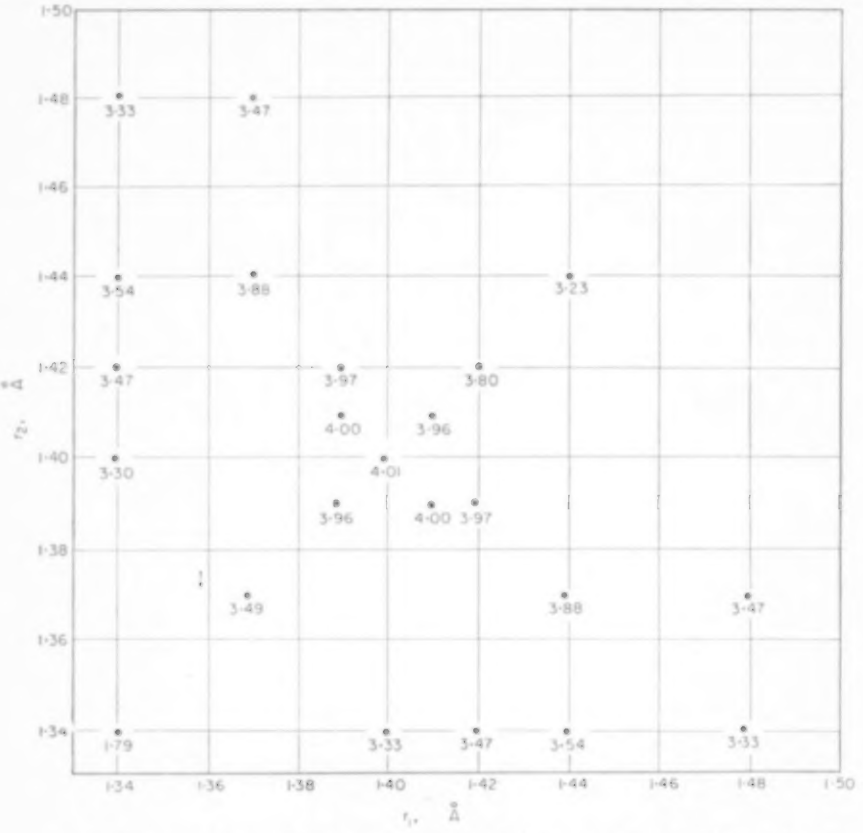


FIG. 4. Calculated values of the total energy $-E(r_1,r_2)$ for benzene, using Kekulé + Dewar structures. The zero of energy is taken at $E = -120$ kcal/mole.

weight. The secular determinant is a 3×3 determinant. This has already been given by Coulson and Altmann[5] in equation (3) of their paper. We have verified that this is correct. In our symbols it is

$$24x^3 - 4(J_1 + J_2)x^2 - 2\{3(J_1 - J_2)^2 + 4J_1J_2\}x + (J_1 - J_2)^2(J_1 + J_2) = 0 \qquad (17)$$

where $6x = 3Q_1 + 3Q_2 - E_\pi$.

By choosing various combinations of r_1 and r_2 this equation can be solved numerically, and $E_\pi(r_1,r_2)$ obtained. By addition of $E_\sigma(r_1r_2)$ we obtain the total energy $E_{\text{total}}(r_1r_2)$. A typical set of such values is shown in Fig. 4. It is at once clear that the equilibrium value $r_1 = r_2 = 1{\cdot}40$ Å is the position of stable equilibrium, though the curve is much flatter along the line $r_1 + r_2 = 2{\cdot}80$ than along the line $r_1 = r_2$. This is just what we

should expect from the known force constants of benzene in the two corresponding normal modes B_{2u} and A_{1g} respectively.

III

In the case of C_8H_8, there are 2 Kekulé structures and 8 Dewar structures, which divide up as in IV, where we have simplified the diagrams by only representing the π-electrons.

IV

The secular determinant is of order 4×4 and the equation for the energy is

$$2048x^4 - 160(J_1 + J_2)x^3 - 20\{24(J_1 - J_2)^2 + 23J_1J_2\}x^2$$
$$+ 28(J_1 + J_2)\{2(J_1 - J_2)^2 + J_1J_2\}x - J_1J_2\{7(J_1 - J_2)^2 - 20J_1J_2\} = 0 \quad (18)$$

where, now

$$8x = 4Q_1 + 4Q_2 - E_\pi \quad (19)$$

A check on (18) may be found from the fact that it gives correct values when $J_1 = J_2$ and when $J_2 = 0$. The significance of $(J_1 - J_2)^2$, which depends on the degree of bond alternation, is very clear.

Fig. 5(a) shows a set of values of $E_{tot}(r_1,r_2)$ for various r_1 and r_2. Along the line $r_1 = r_2$ we have a minimum energy at $r_1 = r_2 = 1{\cdot}404$ Å. But Fig. 5(b), which shows the variation of energy along the line AB, where $r_1 + r_2 = 2{\cdot}81$ Å, suggests that the point (1·404, 1·404) is really a saddle point, and the stable configurations are at (1·375, 1·435) and (1·435, 1·375). Thus we predict a bond alternation with difference 0·06 Å. This is of the same order as that predicted by Longuet-Higgins and Salem[8], but rather larger.

In the case of n = 5, there are three types of Dewar structure:

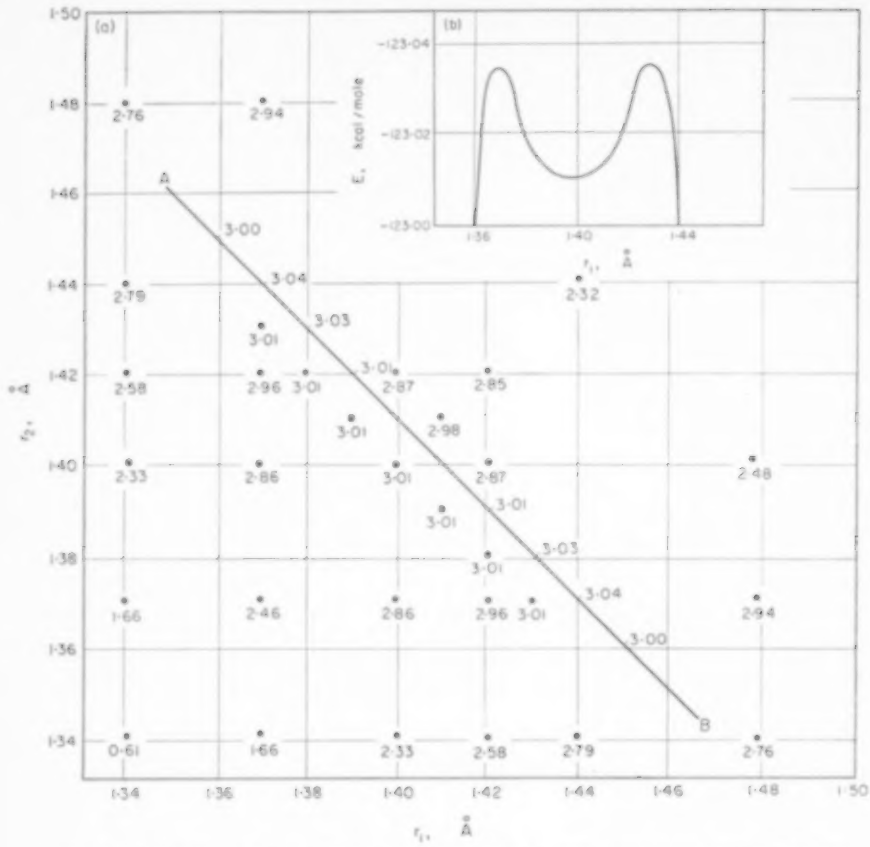


FIG. 5. Main diagram (a). Calculated values of the total energy $-E(r_1,r_2)$ for hypothetical planar C_4H_4, using Kekulé + Dewar structures. The zero of energy is at $E = -120$ kcal/mole. Small inset diagram (b). Curve showing total energy along the line AB of (a), i.e. where $r_1 + r_2 = 2{\cdot}81$ Å. The minimum energy occurs at $r_1 = 1{\cdot}37$, $r_2 = 1{\cdot}44$ Å, and the equivalent position $r_1 = 1{\cdot}44$, $r_2 = 1{\cdot}37$ Å.

The secular determinant is of order 5×5 and the equation for the energy eventually reduces to:

$$\begin{aligned} &31x^5 - 11(J_1 + J_2)x^4 - x^3(738\{J_1^2 + J_2^2\} - 846J_1J_2) \\ &\quad + x^2(J_1 + J_2)(682\{J_1^2 + J_2^2\} - 1018J_1J_2) \\ &\quad + x[1043\{J_1^4 + J_2^4\} + J_1J_2\{7182J_1J_2 - 3302(J_1^2 + J_2^2)\}] \\ &\quad + (J_1 + J_2)[J_1J_2\{1730(J_1^2 + J_2^2) - 4470J_1J_2\} - 335(J_1^4 + J_2^4)] = 0 \end{aligned} \quad (20)$$

where

$$10x = 5Q_1 + 5Q_2 - E_\pi \quad (21)$$

This equation was checked by putting $J_1 = J_2$, when it is divisible by the equation derived *ab initio*
viz.

$$31x^3 - 22Jx - 444J^2x + 560J^3 = 0 \quad (20a)$$

The quintics obtained on inserting numerical values for J_1, J_2 were solved by means of the Oxford 'Mercury' electronic computer, and the energy surface (symmetrical about $r_1 = r_2$, of course) plotted. (Fig. 6).

It turns out that there is a much more definite minimum in this case (n = 5) than in the case n = 4. This occurs at $r_1 = 1{\cdot}365$ Å, $r_2 = 1{\cdot}455$ Å leading to a difference

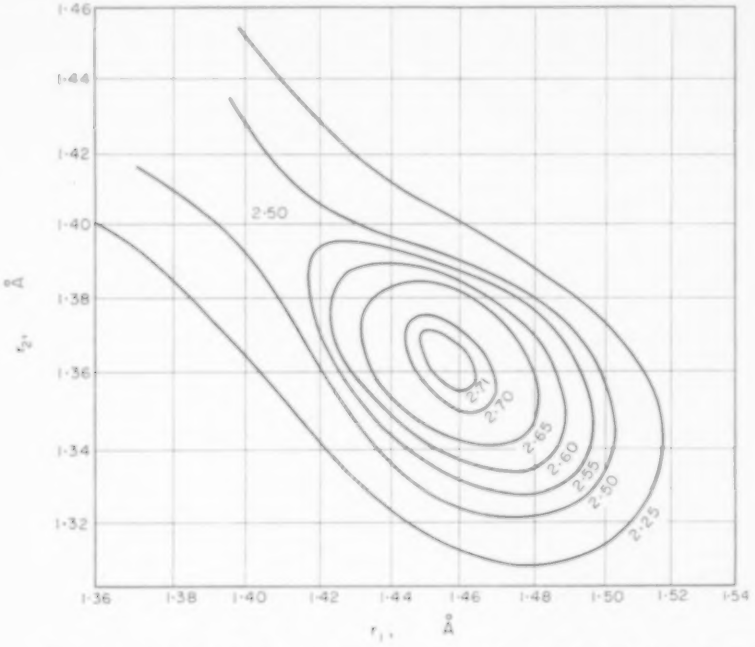


FIG. 6. Calculated values of the total energy $-E(r_1,r_2)$ for hypothetical planar $C_{10}H_{10}$, using Kekulé and Dewar structures. The zero of energy is taken, as in Fig. 5, at $E = -120$ kcal/mole.

of 0·09 Å in the two bond lengths. From this result, it would appear that bond alternation tends to increase with the size of the rings (i.e. when including singly-excited structures in the calculation). It seems to us rather unlikely that subsequent addition of doubly-excited and higher structures would materially alter this. But it should be mentioned that the inclusion of the Dewar structures has led to a distinct change in the bond lengths: for a similar calculation using only the two Kekulé structures leads to bond lengths not greatly different from the values 1·51 and 1·34 Å appropriate to non-resonating single and double bonds.

The difference in energy between the unsymmetrical and symmetrical structures can be seen, from Fig. 6, to be about 0·2 kcal. This, although quite definite, is not large, so that molecules of this kind would show rapid interconversion at room temperature. Further, since the interconversion motion would be slow at the saddle point, an X-ray diagram might easily show an apparently symmetrical appearance.

5. CONCLUSION

The discussion just given seems to us to show that in many respects the v.b. technique leads to very similar results to the m.o. technique, when applied to cyclic

polyenes $C_{2n}H_{2n}$. Small members of this series will tend to have equal bond lengths, but larger ones will definitely show alternation. With Kekulé structures only it is found that beyond $2n = 8$ there is very little resonance, so that one of the two structures dominates the complete wave function. Even in the symmetrical configuration the resonance (more strictly, delocalization) energy is much smaller than in benzene. Inclusion of Dewar structures tends to favour more nearly equal bond lengths, but bond alternations of the order of 0·1 Å may occur.

Note added in proof: Since the manuscript was written, we have included doubly-excited structures in the description of the eight and ten membered rings. This makes almost no difference to the calculated bond lengths in the equilibrium configurations.

Tetrahedron, 1962, Vol. 17, pp. 229 to 233. Pergamon Press, Ltd. Printed in Northern Ireland

VOL. 17 1962

THE CARBON–CARBON TRIPLE BOND AND THE NITROGEN–NITROGEN TRIPLE BOND*

LINUS PAULING
California Institute of Technology, Pasadena, California, U.S.A.

Abstract—The unshared-pair orbital of a nitrogen atom in :N≡N: is estimated to have 21 per cent *p* character and 79 per cent *s* character. The nature of this orbital is such that the energy of repulsion between unshared pairs for the nitrogen–nitrogen triple bond is expected to be very small, whereas it is large, about 40 kcal/mole, for N—N and N=N; in consequence the triple bond is especially stable. For—C≡C—, on the other hand, there is significant repulsion energy of the electrons involved in the adjacent single bonds, causing instability of the triple bond.

THE carbon–carbon triple bond may be described as involving three bent bonds, with the bond orbitals for the three bent bonds as well as the fourth (outer) bond approximately tetrahedral orbitals, with 25 per cent *s* character, about 44 per cent *p* character, 4 per cent *d* character, and 2 per cent *f* character.[1] This description and also the corresponding description of the carbon–carbon double bond are compatible with the observed values of bond lengths and bond angles and of some other properties of substances containing these bonds.

There is, however, an interesting irregularity[2] in the values of the bond energy for the sequence C—C, C=C, C≡C in comparison with the sequence N—N, N=N, N≡N. An explanation of the irregularity is proposed in the following paragraphs.

It is seen from Fig. 1 that the C≡C bond and the N≡N bond have bond energies greater than those of the corresponding single bonds by the same amount, 63 ± 1 kcal/mole. If the same difference in energy held also for the additional bond in the triple bonds, their bond energies would be 210 kcal/mole for C≡C and 163 kcal/mole for N≡N. The observed values are 194 kcal/mole and 226 kcal/mole, respectively; the nitrogen–nitrogen triple-bond energy is 32 kcal/mole less than the carbon–carbon triple-bond energy, rather than 47 kcal/mole greater, as might be expected from the values for the double bonds and single bonds. The anomaly to be accounted for is thus 79 kcal/mole.

This anomaly is related to an anomaly in sequences of values of single-bond energies that has been discussed by Pitzer[3]. For C—C, Si—Si, Ge—Ge, Sn—Sn the values of the single-bond energies, 83, 42, 38, and 34 kcal/mole, respectively, decrease in a reasonable way with increase in period number. For each of the other sequences the value for the first-row element is very small, smaller than for its second-row congener: 38, 51, 32, 30 for N—N, P—P, As—As, Sb—Sb; 33, 51, 44, 33 for O—O, S—S, Se—Se, Te—Te; and 37, 58, 46, 36 for F—F, Cl—Cl, Br—Br, I—I. Pitzer pointed out that the difference between C—C on the one hand and N—N, O—O, and F—F on the other is that the atoms N, O, and F have one or more unshared electron pairs, whereas carbon has only shared electron pairs in its valence shell, and that the

* Contribution No. 2677 of the Gates and Crellin Laboratories of Chemistry.

[1] L. Pauling, *Proc. Nat. Acad. Sci. U.S.* **44**, 211 (1958); *Theoretical Organic Chemistry, Kekulé Symposium* pp. 1–7. Butterworths, London (1958).
[2] L. Pauling, *The Nature of the Chemical Bond* (3rd Ed.) p. 191. Cornell University Press, New York (1960).
[3] K. S. Pitzer, *J. Amer. Chem. Soc.* **70**, 2140 (1948).

repulsion of the unshared pairs causes the bond energy to be abnormally small for N—N, O—O, and F—F. He attributed the absence of a similar strong repulsion of unshared pairs in P—P, etc., to large values of the interatomic distance caused by repulsion of inner shells. Pitzer did not discuss the triple-bond anomaly described above.

This anomaly cannot be attributed to a difference in the bond orbitals of the bent bonds that constitute the triple bonds. It is true that the orbitals are somewhat

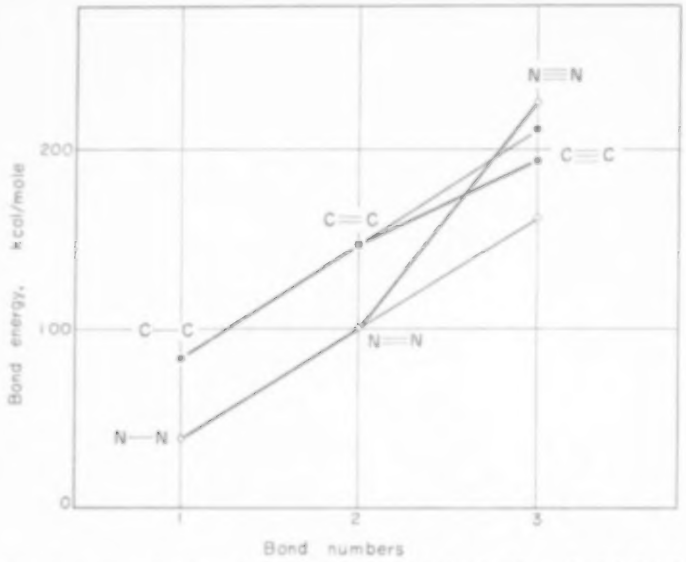


FIG. 1. Experimental values of bond energies for single, double, and triple bonds between carbon atoms and between nitrogen atoms. For triple bonds the values obtained by linear extrapolation from the single-bond and double-bond values are also shown.

different: for carbon they are tetrahedral bond orbitals and for nitrogen they are *p* orbitals with only a small amount of *s* character, about 7 per cent as estimated by a rough calculation[4] and detailed quantum-mechanical treatments.[5] (The *d* character and *f* character are ignored in the following discussion, which would not be changed much by their inclusion.) The maximum strength of this *sp* hybrid bond orbital for nitrogen, 1·93, is a little less than that of the sp^3 tetrahedral orbital for carbon, 2·00, and the nodal angle, 99°, is also less than the tetrahedral angle, 109·5°. These differences should not affect the bond energy greatly, and in particular should not affect the triple bond in a strikingly different way from the double bond.

There is, however, a significant difference in nature between acetylene and the nitrogen molecule: the fourth orbital of each of the carbon atoms in acetylene is a bond orbital, used in the C—H bond, whereas the fourth orbital of each nitrogen atom in N_2 is occupied by an unshared pair of electrons, and this fourth orbital differs greatly from the bond orbitals in such a way as to affect the N—N and N=N bonds differently from the N≡N bond.

[4] Ref. 2, p. 120.
[5] R. S. Mulliken, *J. Phys. Chem.* **56**, 295 (1952); C. W. Scherr, *J. Chem. Phys.* **23**, 569 (1955).

The unshared-pair orbital accompanying three *s–p* bond orbitals with 7 per cent *s* character has 79 per cent *s* character and 21 per cent *p* character. It has no nodal cone (which appears first at 25 per cent *p* character), but has a very small value at 180° from the direction of its maximum (Fig. 2).

Let us consider the interactions of the electrons of two atoms A and B that are not involved in the A—B bond. For ethane, for example, these are the three electrons of carbon atom A that are involved in the C—H bonds to the three hydrogen atoms

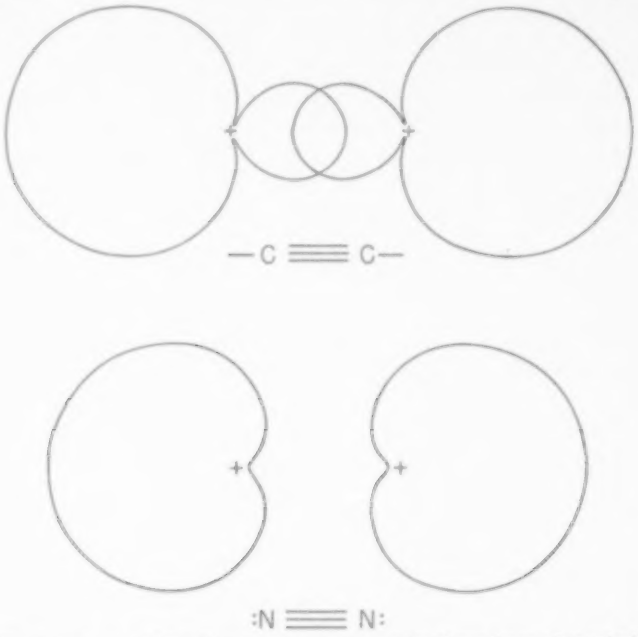


FIG. 2. The upper part of the diagram shows the angular dependence of tetrahedral bond orbitals for the single bonds of two carbon atoms connected by a triple bond. The large lobes extending outwards are involved in overlap with the hydrogen-atom orbitals in acetylene. The small lobes, extending inwards, overlap to produce repulsion, decreasing the energy of the carbon-carbon triple bond. The lower part of the diagram shows the angular distribution for the nitrogen orbitals occupied by unshared pairs in the nitrogen molecule. These orbitals are assumed to have 21 per cent *p* character. The angular distribution is such that there is little repulsion between the two unshared pairs in the nitrogen molecule, but large repulsion between these pairs in molecules in which two nitrogen atoms are connected by a double bond or a single bond.

attached to atom A and the three corresponding electrons for the other carbon atom B. Each of the three electrons of atom A interacts with each of the three electrons of atom B in such a way as to introduce an exchange integral into the energy expression with the coefficient $-1/2$ (in place of $+1$ for two electrons involved in the formation of a shared-electron-pair bond).

These interaction terms are not large, although they are presumably large enough to produce the potential maxima of about 3 kcal/mole restricting rotation about the C—C bond.[1] Their magnitude may be estimated from the strength of the two orbitals concerned along the bond direction. For a tetrahedral orbital the nodal angle is the tetrahedral angle, and hence the strength of the orbital is zero in this direction, and the exchange integral and the interaction energy are expected to be small. For

ethylene, too, the direction of the double bond lies close to the nodal cone for the two carbon orbitals involved in C—H bonds and the strength of these orbitals in the double-bond direction (122° from the C—H direction) is small, so that the interaction energy of these electrons should not change the energy of the C═C bond very much.

In acetylene, however, the two carbon orbitals involved in the C—H bonds have their rather large negative lobes pointed directly toward one another, as shown in Fig. 2, and hence their interaction should decrease the C≡C bond energy considerably.

With the exchange integral taken as roughly proportional to the product of the strengths of the orbitals along the internuclear direction, its value is seen to be $\frac{1}{4}$ of the value of the integral with overlapping of the large lobes (with $S = 2$, compared with -1 for the small lobes). With the factor $-\frac{1}{2}$ in the quantum mechanical energy-expression, the interaction energy of repulsion of these electrons becomes one eighth of that corresponding to maximum overlap. For the distance 1·54 Å the exchange integral may be roughly approximated at 83 kcal/mole, the energy of the single bond. However, a larger value of the exchange integral should probably be used, corresponding to the smaller carbon–carbon distance, 1·20 Å. It is difficult to make a thoroughly reliable estimate of the factor to be used for this correction, but the relation between bond energy, bond number, and bond length for fractional bonds ($n < 1$) indicates that the factor 3 should be used.[6] This leads to 31 kcal/mole for the repulsion energy of the two electrons occupying the outer orbitals of the two carbon atoms in acetylene. The same calculation with orbitals with 25 per cent *s*, 69 per cent *p*, 4 per cent *d*, and 2 per cent *f* character (strength 2·76 for positive lobe, −0·86 for negative lobe) leads to 15 kcal/mole. This effect may accordingly explain the difference 16 kcal/mole between the value 194 kcal/mole for the C≡C bond energy and the value 210 kcal/mole obtained by extrapolation of C—C and C═C.

For nitrogen–nitrogen bonds the principal repulsion is that between the unshared pairs of electrons of the two nitrogen atoms, for which the exchange integral has the coefficient −2. The ratio of the square of the strength of the unshared-pair orbital (Fig. 2) in the triple-bond direction to the square of the strength of the nitrogen bond orbital is 0·0012, and the energy of repulsion of the unshared pairs in the N_2 molecule is hence calculated to be 0·5 kcal/mole. The correction is accordingly very small.

For N—N and N═N the energy of repulsion is much larger, in agreement with the argument advanced by Pitzer[3]. It is difficult to make reliable calculations because of the rapid change of orbital strength with angle and uncertainty about the angle between the orbital axis and the bond direction. A rough calculation gives about 40 kcal/mole for both N—N and N═N (including both unshared pairs and outer bond orbitals), in approximate agreement with indication from the congener sequences.

Although this simple treatment does not permit a reliable quantitative calculation to be made, it seems justified to conclude that the bond energies for N—N and N═N are low because of large repulsion-energy terms involving the unshared electron pairs, and that the relative stability of the :N≡N: triple bond is to be attributed to the smallness of the repulsion between the unshared pairs.

The suggestion made by Pitzer[3] that an increased interatomic distance caused by repulsion of inner shells is the explanation of the apparent absence of unshared-pair repulsion for P—P and similar bonds is, I think, to be rejected. For the same kinds

[6] Ref. 2, pp. 231, 400.

of hybrid bond orbital and hybrid unshared-pair orbital for phosphorus as for nitrogen, the ratio of unshared-pair repulsion energy to bond energy should be the same for P—P as for N—N. If, however, the hybrid character of the phosphorus orbitals were different from that of the nitrogen orbitals in such a way as to permit the unshared pair to swing farther away from the adjacent bonded atoms, the repulsion energy would be greatly decreased. This difference in hybrid character could involve a larger contribution of the *d* orbital for phosphorus than for nitrogen; and, indeed, a much larger contribution of 3*d* to the 3*s*3*p* hybrid orbitals for phosphorus is to be expected than of 3*d* to 2*s*2*p* for nitrogen, because of the far smaller promotion energy involved. I doubt that repulsion of inner shells is of much significance in bonds such as P—P.

VOL. 17 1962

Tetrahedron, 1962, Vol. 17, pp. 235 to 237. Pergamon Press, Ltd. Printed in Northern Ireland

ON THE NATURE OF BONDS BETWEEN CARBON ATOMS

INGA FISCHER-HJALMARS
Division of Mathematical Physics, The Royal Institute of Technology, Stockholm 70

(*Received* 16 *February* 1961)

VOL. 17 1962

Abstract—The combined effect of conjugation and van der Waals' interaction has been calculated for carbon sp^2–sp^2 single bonds of different lengths and for different molecular conformations. The bond shortening effect of conjugation is found to be comparable to that of hybridization. The attractive van der Waals' interaction, on the other hand, is always found to be small. It seems thus most improbable that this interaction should be the cause of the planarity of butadiene.

IT seems to be fairly generally recognized that the distance between bonded atoms is governed by several factors: electron delocalization, hybridization, electronegativity, steric effects, etc. Especially for bonds between carbon atoms, the electronegativity differences should be of minor importance. In a recent paper Bak and Hansen-Nygaard[1] (see this paper for references to other recent publications in this field) have discussed the combined effect of changes in hybridization status and electron delocalization on the length of bonds between carbon atoms. From experimental data for such molecules, where the bond distance is essentially determined by hybridization, atomic covalent radii can be derived. Bak *et al.*[1] suggest the following values of single bond, covalent radii of carbon: $r_C(sp^3) = 0{\cdot}7723$, $r_C(sp^2) = 0{\cdot}7587$, $r_C(sp) = 0{\cdot}7333$. In the present note a few data in support of this assignment will be discussed and the combined effect of electron delocalization, i.e. conjugation, and steric repulsion will be considered.

Table 1 gives the experimental values of the length of the sp^2–sp^2 single bond, connecting two π-electron systems, and of the twist angle around this bond.

TABLE 1

Substance	Bond length (Å)	Twist angle
1,3-Butadiene[2]	1·483	0°
Biphenyl[3]	1·490	42°
Hexaphenyl benzene[4]	1·515	90° ± 10°
$2 \times r_C(sp^2)$	1·517	

It has been suggested previously by Adrian[5] that experimental values of the twist angle in similar molecules depend on a minimum of the potential curve (energy vs. angle), obtained from the combined effect of conjugation and steric repulsion between the two parts of the molecule, connected by the single C—C bond. The present

[1] B. Bak and L. Hansen-Nygaard, *J. Chem. Phys.* **33**, 418 (1960).
[2] A. Almenningen, O. Bastiansen, and M. Trätteberg, *Acta Chem. Scand.* **12**, 1221 (1958).
[3] A. Almenningen and O. Bastiansen, *Kgl. Norske Vid. Selsk. Skr.* No. **4** (1958).
[4] A. Almenningen, O. Bastiansen and P. N. Skancke, *Acta Chem. Scand.* **12**, 1215 (1958); private communication by Skancke.
[5] F. J. Adrian, *J. Chem. Phys.* **28**, 608 (1958).

author would like to modify this suggestion slightly by considering the combined effect of conjugation and a more general van der Waals' interaction. Moreover, it is suggested that a correlation could be found between the depth of this potential minimum and the length of the bond around which the molecule is twisted.

In order to find this correlation one must know the angular dependence of the van der Waals' interaction and of the energy of conjugation across the single bond. The van der Waals' interaction between molecules has been extensively investigated and can be computed according to different, more or less accurate formulae.[6] These formulae may be modified to be applicable to intra-molecular van der Waals' interaction, giving at least the correct order of magnitude. Hill[7] has, however, derived a special formula for the intra-molecular case, which seems to give the most accurate estimate of this effect. In the present study only the van der Waals' interaction between

TABLE 2. COMBINED EFFECT OF CONJUGATION AND STERIC FORCES. ENERGIES IN kcal/mole

Substance	Twist angle (conformation)	van der Waals' interaction	Conjugation energy	Combined effect
Butadiene	0° (*trans*) (min)	−0·10	−9·0	−9·1
	90°	−0·08	0	−0·1
	180° (*cis*)	+1·18	−9·5	−8·3
Biphenyl	0°	+1·49	−3·9	−2·4
	24° (min)	+0·23	−3·3	−3·0
	42°	−0·10	−2·2	−2·3
	90°	−0·04	0	−0·0
Hexaphenyl benzene, antipropeller model	90°	−0·25	0	−0·2
	80° (min)	−0·32	−0·7	−1·0
	70°	+17·51	−2·7	+14·8

the hydrogen atoms of the two parts of the molecule has been investigated. In the cases of butadiene and biphenyl it is obvious from a study of steric models of these molecules that the H—H interactions are the only important ones. In the case of hexaphenyl benzene this is also true for the "antipropeller" model (*cf.*[4]) but not so for the "propeller" model, where steric interaction between the carbon rings is important. Because of the difficulty in obtaining parameter values for this kind of interaction, only the "antipropeller" model has been studied at present.

The estimate of the angular dependence of the conjugation energy is considerably more difficult. This question has been discussed in detail by Adrian,[5] who has developed a method for this estimate, based on the valence bond treatment. He has also applied his method to a number of molecules, including biphenyl. Furthermore, the general interaction of two conjugated systems has been investigated by Longuet-Higgins and Murrell[8] on the basis of the molecular orbital method. They have applied their method *inter alia* to butadiene and biphenyl, but only to the extreme

[6] J. O. Hirchfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*. John Wiley, New York (1954).
[7] T. L. Hill, *J. Chem. Phys.* **16**, 399 (1948).
[8] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.* **68**, 601 (1955).

cases of either coplanar or perpendicular conjugated systems. On the basis of their method the present author has made a rough estimate of the energy in intermediate cases. The details of this method and a comparison with Adrian's method will be published in a forthcoming paper, where all details of the present calculations will be given. The results of these calculations are listed in Table 2.

A few comments should be made on the values of Table 2. The values of conjugation energy are taken from theoretical calculations of electronic spectra.[8] These values are not always in accordance with conjugation energy values determined more directly from empirical data.[9] In the case of butadiene for instance, the "empirical" value is only half as large as the theoretical one. Hence, it is not advisable to try to find a correlation between bond length and potential minimum by aid of the values of Table 2 only. Nevertheless, these two quantities are listed together in Table 3.

VOL. 17 1962

TABLE 3

Substance	Bond length (Å)	Potential minimum (kcal/mole)
Butadiene	1·483	−9·1
Biphenyl	1·490	−3·0
Hexaphenyl benzene	1·515	−1·0

Table 2 shows unquestionably that the van der Waals' interaction cannot be the cause of the planarity of butadiene, since this interaction has almost the same value for the perpendicular conformation as for the *trans*-conformation. Moreover, Table 2 indicates that biphenyl is most likely non-planar, although the potential hill of the planar conformation is very low (0·6 kcal/mole). All conformations between 0° and 40° seem to be comparatively easy of access at room temperature. As for hexaphenyl benzene, finally, the most stable conformation should be close to the perpendicular one. These results agree reasonably well with the experimentally determined twist angles of Table 1.

The only comment that at present could be made on the values of Table 3 is that the deeper potential minima correspond to the shorter bond distances and that the bond shortening effect of conjugation seems to be of a magnitude comparable to that of hybridization.

[8] G. W. Wheland, *Resonance in Organic Chemistry*. John Wiley, New York (1955).

Tetrahedron, 1962, Vol. 17, pp. 239 to 241. Pergamon Press Ltd. Printed in Northern Ireland

VOL. 17 1962

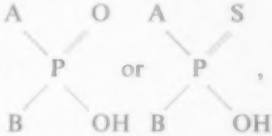
CONJUGATION IN SYSTEMS WITH A TETRAHEDRAL ATOM—DIARYLPHOSPHINIC ACIDS

M. I. KABACHNIK, T. A. MASTRYUKOVA and T. A. MELENT'YEVA
The U.S.S.R. Academy of Sciences, Moscow

(*Received* 3 *April* 1961)

OF the two methods for the transmission of the mutual influence of atoms—by chain induction and by conjugation—only the latter is determined by steric factors. π-Bonds must be coplanar. The influence of an unsaturated substituent coupled to the reaction centre by a system of conjugated bonds sharply diminishes when it is removed from the plane of the system, for example, through steric hindrance, which is shown in the physical properties of the substances and in the velocity and equilibrium constants of their chemical reactions. This phenomenon has acquired the name of the secondary steric effect.

On $\delta\rho$ analysis, the secondary steric effect leads to a deviation from the linear relationship $\log \frac{k}{k_0} = \rho\delta$, which is connected with a change in the value of δ on disturbing the conjugation of the substituent with the transmitting chain and the reaction centre.[1]

It was found earlier that, on $\delta\rho$ analysis of the influence of a substituent on the strength of acids of phosphorus of the general type  or , the linear relationship $pk = pk_0 - \rho\Sigma\delta$ in various media was well maintained for oxyacids and thioacids of phosphorus with the most diverse substituents A and B,[2–6] except for the case in which both substituents A and B are phenyl or *p*-tolyl groups.[3] It was shown, in fact, that δ for a phenyl group has a constant value of $-0{\cdot}481$ with any second substituent on the phosphorus atom: hydroxyl, alkyl or substituted alkyl, alkoxyl, aroxyl, etc, but changes to $-0{\cdot}592$ in the case where the second substituent on the phosphorus is also a phenyl group.

For the *p*-tolyl group, the value of δ, $-0{\cdot}602$ with any of the substituents enumerated above, changes to $-0{\cdot}723$ when two tolyl groups are present in the molecule.

To explain this phenomenon it was postulated that this change in the value of δ for phenyl and *p*-tolyl when two such groups are present in the molecule is connected

[1] R. U. Taft. Paper in the symposium *N'yamena Prostranstvennyye effekty v organicheskoi khimi* [Steric Effects in Organic Chemistry] pp. 581–584. Foreign Literature Publishing House, Moscow (1960).
[2] M. I. Kabachnik, *Dokl. Akad. Nauk SSSR* **110**, 393 (1956).
[3] T. A. Mastryukova, T. A. Melent'yeva, A. E. Shipov and M. I. Kabachnik, *Zh. Obshch. Khim.* **29**, 2178 (1959).
[4] M. I. Kabachnik, T. A. Mastryukova, A. E. Shipov and T. A. Melent'yeva, *Dokl. Akad. Nauk SSSR* **124**, 1061 (1959).
[5] M. I. Kabachnik, T. A. Mastyukova, A. E. Shipov and T. A. Melent'yeva, *Tetrahedron* **9**, 10 (1960).
[6] M. I. Kabachnik, S. T. Ioffe and T. A. Mastryukova, *Zh. Obshch. Khim.* **30**, 2763 (1960).

with a steric disturbance of the conjugation of the π-electrons of the system of aromatic rings with the P═O bond.

The idea of the steric disturbance of conjugation in the case under consideration needs to be specified somewhat more precisely.

The usual phenomena of this type are associated with the steric hindrance of coplanarity. This is the case in the disturbance of conjugation in purely carbon

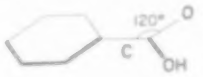


FIG. 1. sp^2 hybridization and conjugation; benzoic acid; the atoms of the benzene ring and the CO_2 group lie in the same plane.

π-bond systems, in which, as is well known, conjugation ensures the planarity of the arrangement of substituents about the sp^2 hybridized carbon atom (Fig. 1). In the case of the diarylphosphonic acids, the central multiple-bonded phosphorus atom retains its tetrahedral configuration (sp^3 hybridization; one unhybridized *d*-electron takes part in the π-bond). Hence, of the two phenyl rings bound to the phosphorus atom, only one can be coplanar with the plane of symmetry of the electron cloud of

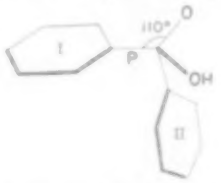


FIG. 2. sp^3 hydridization and conjugation; diphenylphosphinic acid; the atoms of benzene ring (I) and the P═O group lie in the same plane; the atoms of benzene ring (II) and the P═O group lie in a different plane intersecting the first along the axis of the P═O bond.

the P═O π-bond. The second ring lies in another plane intersecting the plane of the conjugated system along the axis of the P═O bond (Fig. 2). According to a second alternative, both phenyl rings are non-coplanar with the plane of symmetry of the P═O π-bond, the planes of the rings intersecting it at equal or unequal angles.

In monophenylphosphinic acid and its hydrogen esters (Fig. 3), the plane of symmetry of the P═O π-bond can always be orientated in coplanarity with the plane

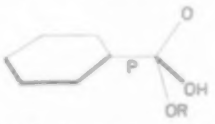


FIG. 3. Phenylphosphinic acid and its hydrogen esters; the atoms of the benzene ring and the P═O group lie in the same plane; the OH and OR groups are at the apices of a tetrahedron.

of the benzene ring. When the conjugation is disturbed, the value of δ for the phenyl ring must diminish, approaching the value of δ for alkyl groups. In diphenylphosphinic acid, one of the phenyl rings (or both) is present under conditions less favourable for conjugation than in the monophenyl derivative; this must lead to a diminution in the value of δ to some value characterizing the mean degree of disturbance of the conjugation. Experiment shows that this change amounts to approximately 20 per cent of the basic magnitude of δ.

The fact that this change is not connected with the steric hindrance of coplanarity is shown by the absence of the effect with a branched alkyl radical (isopropyl or cyclopentyl) in place of the second aromatic group; in these cases no deviation from the linear relationship $pk = pk_0 - \rho\Sigma\delta$ is observed when the usual value of δ for a phenyl group is employed (−0·481). It follows from this that the disturbance of the conjugation is a phenomenon specific to the simultaneous presence of two aromatic (or possibly, in the general case, unsaturated) substituents on the phosphorus.

It is of interest to note that when two different aromatic substituents are introduced (for example, phenyl and *p*-tolyl), good agreement with Hammett's equation is obtained with the use of the values of δ deduced from the symmetrical acids (that is, 0·592 for the phenyl group and 0·723 for the tolyl group).

Thus, when a second aromatic grouping is attached to the phosphorus atom, a regular change in the value of the constant δ, connected with a disturbance of the conjugation, is observed.

The phenomenon considered must be extremely general for π-conjugated aromatic or unsaturated systems including an atom with a tetrahedral (or other non-planar) distribution of bonds.

VOL. 17 1962

Tetrahedron, 1962, Vol. 17, pp. 243 to 246. Pergamon Press Ltd. Printed in Northern Ireland

REMARKS CONCERNING THE EFFECT OF ENVIRONMENT ON THE PROPERTIES OF CC AND CO BONDS

R. DAUDEL
Centre de Mécanique Ondulatoire Appliquée
155 Rue de Sévres, Paris

VOL. 17 1962

Abstract—The purpose of this paper is to present, in a simple way, some results recently obtained at the "Centre de Mécanique Ondulatoire Appliquée" in studying the effect of environment on CC and CO bonds.

RELATION BETWEEN NOTATION AND LENGTH OF AROMATIC CC BONDS

THE effect of the environment of a bond can be divided into two classes:

(a) that which comes from nearest neighbours,

(b) that which comes from other parts of the molecule.

The latter is only important if the molecule contains delocalized bonds, arising either from conjugation or hyperconjugation.

The effects of the neighbourhood of the bond are very often classified as follow:

(1) Influence of the number and the organization of electrons surrounding the cores of the atoms of the bond (roughly the hybridization effect).

(2) Effect due to the charges of other cores surrounding the bond (inductive effect).

(3) Interaction between non-bonded atoms.

Until now it has not been possible to aportion satisfactorily the role of each individual effect.

Following Pauling, Mulliken and others it has become customary to explain in terms of conjugation and hyperconjugation the various CC bondlength which are found in molecules containing delocalized bonds.

More recently Dewar and Schmeising[1] have found that all evidence for the existence of appreciable effects of π-electron resonance in the ground states of conjugated and hyperconjugated molecules is inconclusive and that all observed effects can be explained as a result of differences in hybridization in carbon σ bond orbitals. Mulliken[2] has discussed Dewar's arguments and has shown that if the effect of resonance is probably not as great as has been usually supposed, it is nonetheless, not entirely negligible.

On the other hand Bartell[3] believes that the interaction between non-bonded atoms (which is the most neglected factor) gives promise of becoming one of the most important. He has shown that if a plausible set of potential functions describing interactions between non-bonded atoms are used, carbon–carbon bond lengths in non-aromatic hydrocarbons can be closely computed without invoking hybridization, conjugation or hyperconjugation.

However, Wilson[4] has strong objections against this point of view.

In such a confused situation it has seemed desirable to reconsider the notion of

[1] M. J. S. Dewar and A. N. Schmeising, *Tetrahedron* **5**, 166 (1959).
[2] R. S. Mulliken, *Tetrahedron* **6**, 68 (1959).
[3] L. S. Bartell, *J. Chem. Phys.* **32**, 827 (1960).
[4] This symposium: E. B. Wilson, Jr., *Tetrahedron* **17**, 191 (1962).

"bond notation" introduced several years ago[5] to represent the effect of environment on the length of an aromatic CC bond. It will be perhaps useful to recall that in an alternant conjugated hydrocarbon "bond notation" has been given to the set of the types of the CC bonds adjacent to a given bond; a bond type refers to the number of CC bonds which are adjacent to a given bond.

Fig. 1 shows, for example, the types of the CC bonds in naphthalene.

FIG. 1.

From this figure, it is obvious that, for example, the notation of the central bond will be (3,3,3,3) and that the notation of an $\alpha - \beta$ bond will be (2,3).

It has been shown[5] that both from the theoretical and from the experimental point of view the length of a CC bond only depends on its notation at least in a first approximation.

TABLE 1

Notation	Bond length (Å)
(2,3)	1·382 ± 0·019
(2,2)	1·397 ± 0·013
(2,4,4)	1·390 ± 0·010
(2,3,4)	1·425 ± 0·025
(3,3,3,3)	1·415 ± 0·021

TABLE 2

Notation	Bond length (Å)					
	B	N	A	C		V
(2,3)	1·397	1·364	1·368	1·361	1·376	1·369 ± 0·008
(2,2)		1·415	1·419	1·392		1·405 ± 0·014
(2,4,4)				1·405	1·423	1·414 ± 0·009
(2,3,4)		1·421	1·436	1·427	1·418	1·427 ± 0·009
(3,3,3,3)		1·418	1·428			1·423 ± 0·005

B = benzene, N = naphthalene, A = anthracene, C = chrysene, V = central value.

Using experimental measurements made before 1955 the lengths that can be associated with some bond notations are given in Table 1.[6] The r.m.s. deviation from the central values is 0·016 Å.

Since that time important refinements have been introduced[7] in the experimental evaluation of bond length, and Table 2 gives the new lengths associated to the same set of bond notations.

The r.m.s. deviation is now only 0·009 Å and shows that the bonds possessing the same notation have the same length, the deviation from that rule being of the order of magnitude of the experimental uncertainty.

[5] C. Vroelant and R. Daudel, *Bull. Soc. Chim. Fr.* **16**, 36 (1949). See also R. Daudel, R. Lefebvre and C. Moser, *Quantum Chemistry, Methods and Applications* p. 128 *Interscience*, New York (1959).
[6] R. Daudel, *Advanc. Chem. Phy.* **1**, 177 (1958).

It is of interest to note that the use of bond notation to predict bond lengths is as precise as the calculations based on MO or VB theory. Cruickshank and Sparks[7] have shown that recent X-ray results for the bond lengths in some alternant hydrocarbons agree to about 0·01 Å with MO and VB theories.

The consistent results of bond notation might be considered to be a proof of the effect of conjugation in determining the bond lengths in aromatic molecules, as the demonstration[5] of the relation between notation and length is based on resonance theory.

However the consistency may also be considered as only an empirical rule, a refinement in a sense of the law observed by Costain anf Stoicheff[8] that state that the C—C, C=C and C—H bond lengths increase linearly with increase in the number of adjacent bonds.

In conclusion we can say that, even in conjugated molecules, the length of a bond only depends on its environment but this includes a larger part of the molecule than in molecules containing only localized bonds.

This extension of the "effective" environment gives, in a sense, a measure of the conjugation effect. Refinements of the structures of many alternant hydrocarbons would be helpful to measure the generality of the above statements.

EFFECT OF ENVIRONMENT ON THE FORCE CONSTANT OF THE CARBONYL GROUP

As for bond distance, the force constant of a bond may also be considered as a measure of its strength. The force constant of a bond is correlated with its stretching vibration frequency which may be determined from the study of the corresponding infra-red spectrum. This is why chemists very commonly use infrared data to ascertain the effect of environment on a given bond. For example, the fact that the $\nu_{C=O}$ stretching frequency is 1775 cm^{-1} for cyclobutanone and about 1715 cm^{-1} for non-cyclic saturated ketones has been considered as evidence of the "unsaturated character" of small rings.

As Bratoz and Besnainou have shown, going directly from the stretching frequency to the structure of the C=O bond is dangerous. It is better to use the force constant as intermediate quantity.

Using Wilson's matrices, or more exactly a perturbation procedure[9] giving more intermediate results, Bratoz and Besnainou[10] have calculated the force constant of the C=O bond in various compounds, like saturated and unsaturated ketones, aldehydes, carbocylic acids, esters and quinones.

Table 3 gives some of their results.

TABLE 3. FORCE CONSTANTS (10^5 dyne/cm)

Saturated ketones	10—10·3
Unsaturated ketones	9—9·8
Halogenated ketones	10·3—10·9
Cyclobutanone	10·3
Orthoquinones	9·7—10·1
Paraquinones	9·5—9·9

[7] D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.* A **258**, 270 (1960).
[8] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* **30**, 777 (1959).
[9] S. Bratoz, *J. Chem. Phys.* **28**, 159 (1955).
[10] S. Bratoz and S. Besnainou, *J. Chim. Phys.* **56**, 555 (1959).

It is interesting to point out that the force constant in cyclobutanone has about the same value as that in non-cyclic saturated ketone. The use of the perturbation method has clearly shown that the increase of the frequency is mainly due to the fact that in cyclobutanone the angle between the C=O and the adjacent C—C bonds is smaller than in an ordinary ketone; this change of geometry increases the coupling between the C=O and the adjacent C—C vibrators. The change of $\nu_{C=O}$ is finally mainly due to a mechanical factor and not to an electronic one. Again, evidence of conjugation disappears.

The most striking effect of the environment shown by Table 3 is the low value ($9 \cdot 10^5$ dyne/cm)of the force constant in some unsaturated ketones and its high value ($10 \cdot 9\ 10^5$ dyne/cm) in some halogenated ketones. To understand the origin of each variation observed on Table 3, Bratoz and Besnainou[11] have determined the π-electronic wave function corresponding to the various molecules concerned using the Pariser and Parr approximation and have given a general formula for the force constant of a bond in that approximation.

To represent the inductive effect of the adjacent atoms of the carbonyl group they have estimated the penetration integrals from the ionization energy of some free radicals. The other necessary parameters used are those of Sidman coming from the ultra-violet spectrum of formaldehyde.

Table 4 compares the force constants calculated using that way and those coming from the stretching frequencies.

TABLE 4. FORCE CONSTANTS (10^5 dyne/cm)

	From electronic wave function	From stretching frequencies
Acetone	10·29	10·3
Formaldehyde	10·58	10·8
Orthobenzoquinone	10·15	10·0
Parabenzoquinone	10·11	9·8

TABLE 5. EFFECT PRODUCING THE SHIFT OF $\nu_{C=O}$

	$\nu_{C=O}$(in cm^{-1})	
Saturated ketones	1706–1725	
Unsaturated ketones	1650–1750	mesomeric effect
Chlorinated ketones	1725–1765	inductive effect
Cyclobutanone	1775	coupling between vibrators
Saturated aldehydes	1720–1740	coupling between vibrators + inductive effect
Quinones	1660–1690	coupling between vibrators + mesomeric effect + inductive effect

The quantitative agreement obtained gives confidence in the final conclusions of the authors which are given in Table 5 and lists the effects on the $\nu_{C=O}$ stretching frequency due to various kind of environment.

[11] S. Bratoz and S. Besnainou, *J. Chem. Phys.* **34**, 1142 (1961). S. Besnainou, Thesis, Paris (1960).

Tetrahedron, 1962, Vol. 17, pp. 247 to 266. Pergamon Press Ltd. Printed in Northern Ireland

VOL.
17
1962

DISCUSSION

Robert S. Mulliken

*General Discussion of Questions raised in the Contributed Papers**

I SHOULD like to make several specific comments in reaction to some of the very interesting articles in this Paper Symposium. Basically, I am in agreement with Bright Wilson's agnostic views about why bond lengths are as they are. I believe that there are a number of big and little reasons which contribute, varying in importance from case to case. This makes it difficult to pick out and assign correct weighing to the real reasons, either in general or in particular cases.

The greatest difficulty of all may be that it is almost impossible for any one individual to collect and to keep in view all at once the now extremely large and very varied mass of both experimental and theoretical evidence, all of which must be most cautiously and critically and simultaneously evaluated if he is to reach sensible conclusions. The whole field is so extensive and so complex, and experiment and theory are so intimately interwoven, that it is easy to overlook or underemphasize relevant considerations, and extremely difficult to obtain and maintain a well-balanced judgment containing a correct proportion of open-minded tentativeness. Perhaps for the moment we should relax a bit. It seems likely that, before long, new experimental data and new theoretical calculations of much increased accuracy will help us to see things more clearly.

Nevertheless, while I am open-minded about new evidence, both experimental and theoretical, I hold rather strongly to the views I have expressed in two recent articles in *Tetrahedron*.[1,2] These papers were written in some haste and are not quite as clearly stated as one might wish. Hence I should like here, along with other comments, to reiterate and try to clarify some of the main points made there.

(1) I should like to emphasize the importance of a due regard for the hierarchies of conjugation and hyperconjugation types, as deduced from either valence-bond or molecular orbital theory, and supported by experimental evidence.[1] Namely, isovalent conjugation should give the largest effects, sacrificial conjugation less, and the same with hyperconjugation. Conjugation effects in any given category should be larger than hyperconjugation effects. Further, we should distinguish homodative, (more or less) non-dative, and dative conjugation or hyperconjugation as effects of diminishing importance in that order.

(2) Lide's paper[3] emphasizes clear evidence for rather large bond length shortenings attributable to dative isovalent conjugation, which means partial electron donation from a π lone pair of a donor group into an unsaturated system. This donor-acceptor action is increvalent from the point of view of the donor group (one new π bond is

* This work was assisted by the Office of Naval Research.

[1] R. S. Mulliken, *Tetrahedron* **5**, 253 (1959).
[2] R. S. Mulliken, *Tetrahedron* **6**, 68 (1959).
[3] D. R. Lide, Jr., This Symposium, p. 125.

formed) but sacrificial from that of the unsaturated system (one carbon atom gets de-bonded); *over-all* it is isovalent.

(3) On the other hand, Lide, in agreement with others, points out clearly that in hydrocarbons, C—C bond lengths can be predicted in most cases within experimental error by assuming a fixed covalent single-bond radius for what are usually considered to be *sp*, sp^2 and sp^3 carbon atoms. In other words, one has indeed a rather reliable and very *simple recipe* for predicting C—C bond lengths in hydrocarbons if one thinks only in terms of hybrid types without considering π-electron delocalization. So far, so good.

But in terms of fundamental understanding, and of the interpretation and prediction of other properties than bond lengths, an open-minded consideration of all the evidence, experimental and theoretical together,[1,2] leaves little doubt that π electron delocalization makes substantial contributions to observed C—C bond shortenings in conjugated and hyperconjugated systems. My best present judgment is that on the whole hybridization contributes somewhat more than electron delocalization to the observed shortenings, but that the two causes are of the same order of magnitude: and that in addition, other causes make contributions which usually are smaller, but sometimes may be fairly important.

An important reason why it is difficult to decide experimentally between hybridization and electron delocalization as causes of bond shortening is the fact that the two effects largely operate in parallel: wherever there is double-bond conjugation, there is a change in hybridization, and when there is triple-bond or cumulene-type conjugation, there is a further change. Under these circumstances, it becomes rather necessary, and proper, to place considerable reliance on theory, provided it is reliable theory. As to the reliability of the theory now being used, this seems rather well buttressed,[2] although there are questions of detail, and perhaps *small* doubts about some major points, so that one must not be too dogmatic. In any event, it is the same delocalization theory that seems clearly *necessary* to explain the observed bond shortenings in dative isovalent conjugation which is used in estimating the effects of electron delocalization in conjugation and hyperconjugation in general.

(4) I am inclined to agree with Dewar that the term conjugation (now extended to include isovalent conjugation, as in benzene) can best be used to denote comprehensively the alterations in chemical and physical characteristics which are found *empirically* in molecules when single bonds are located between double or triple bonds or between the latter and lone-pair donor groups, and so on.[2] Such a phenomenological definition and concept of conjugation seems to be safer and historically better justified than one based on theoretical explanations of the *reasons* for the empirical differences between conjugated and unconjugated systems. Thus, for example, bond shortenings of C—C bonds, *whatever* the cause or causes, may be accepted as characteristic manifestations of conjugation. In such a definition, primary emphasis must, however, be placed on *ground state* behavior, since excited electronic states are many and varied in nature.

Having gone so far, it should nevertheless be noticed that even the most completely empirical definition and concept of conjugation still indispensably involves a definitely theoretical concept, namely that of chemical bonds. The above-discussed supposedly empirical definition of conjugation can be stated only in terms of what happens when various juxtapositions of bonds are present in a molecule, and the existence of bonds,

whether classically or quantum-mechanically conceived, is a theoretical concept. Dewar's concept of conjugation is then apparently no more than *semi-empirical*.

Very similar comments are applicable to the concept of hyperconjugation. Although historically this concept was introduced in a context of theoretical explanation with emphasis on electron delocalization, it would seem to be sounder to use the term to denote the very real changes in chemical and physical properties which are observed to be associated with the presence of methyl or substituted methyl or methylene groups close to π bonds in unsaturated systems. However, I am not at all convinced that it is necessary to abandon the term "hyperconjugation" in favor of a new term "semi-conjugation", as Dewar and Schmeising have recently proposed,[4] merely because the introduction of "hyperconjugation" was accompanied by explanations in terms of electron delocalization.

VOL. 17 1962

The foregoing comments and proposals, made in the interest of clarity of definition, of course do not involve any modification of beliefs as expressed in item (3).

Concerning the subclassification of conjugation and hyperconjugation into isovalent and sacrificial, and dative, homodative and non-dative categories as mentioned in item (1), it may be objected that the adjectives thus introduced are based on theory, and thus are inconsistent with the proposal to regard conjugation and hyperconjugation as semi-empirical concepts. This objection may be countered as follows. (a) I believe that an examination of the empirical properties of each of the sub-classes of molecules distinguished by the various adjectives will show distinctive features, blurred or even concealed, to be sure, by extraneous factors in the case of the weaker types of conjugation and especially hyperconjugation. (b) Granting that there are empirically distinct sub-classes, names are needed to distinguish them. The names adopted have, to be sure, a theoretical origin, but the theory involved goes beyond classical bond theory (which had to be assumed in setting up a semi-empirical concept of conjugation or hyperconjugation) only by making use of the simplest possible, and (in the case of conjugation, at least) generally accepted classically-bonded resonance structures. The main point is that some sort of terminology is needed, and the use of designations based on the theory of resonance between classical bond structures supplies this need in a way which is especially convenient and self-explanatory even if one does not wish to accept all its implications literally. However, I myself see no need to reject at least partial validity of the theoretical implications of the proposed terminology. It is very useful to distinguish sacrificial from isovalent conjugation, and to distinguish dative from other kinds of conjugation. I have found these distinctions most helpful in obtaining better insight into the structures of molecules. An interesting example is a comparison between aniline or phenol; with dative isovalent conjugation, nitrobenzene, with dative sacrificial conjugation, and *p*-nitroaniline, where again there is dative isovalent conjugation.[1] That nitrobenzene is in a different class from the others seems not to be generally realized.

[4] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **11**, 96 (1960). I disagree or have very strong reservations on the main conclusions in that paper, but because of pressure of other work must postpone detailed comments. However, I should like to express sincere regret if I have misinterpreted or misquoted their earlier paper (*cf.* footnotes on p. 97 and p. 101 of their 1960 paper). In explanation, I should like to mention that at the time my paper was written, I had not seen the manuscript of their paper, but was relying on notes I had made based on Professor Dewar's oral presentation and discussion at the 1958 Conference on Hyperconjugation; possibly a subjective element may have somewhat colored these notes.

(5) Much confusion in the literature has, I believe, been generated by the identification of the concept of hyperconjugation with the Baker–Nathan effect.[1] Experimentally they are different concepts, while in terms of the π delocalization theory of hyperconjugation, the Baker–Nathan effect is *not* hyperconjugation, but may be attributable to *differences* between C—C and C—H hyperconjugation, although other causes may be partly or largely responsible. The delocalization theory sees no difference in kind between C—C and C—H hyperconjugation, but admits the possibility of quantitative differences, experimental evidence on which has been elucidated especially by Taft and co-workers.

Historically, the π delocalization theory of what would now be called isovalent hyperconjugation was apparently first used in a 1933 paper of mine on twisted ethylene, while the applicability of the same theory to examples of what would now be called sacrificial hyperconjugation was early recognized by Wheland, and by Hückel. The same idea was also stated briefly in the original paper of Baker and Nathan, but in later papers they restricted the idea to what is now called C—H hyperconjugation, and (perhaps at first tentatively) *assumed* C—C hyperconjugation to be non-existent. Thereby the experimentally observed *differences* between C—C and C—H sacrificial hyperconjugation—the Baker–Nathan effect—became identified with the later-proposed term hyperconjugation. Here it may be recalled that sacrificial hyperconjugation is expected to be a relatively weak effect, so that differences between C—H and C—C sacrificial hyperconjugation should thus be still weaker and easily masked (or simulated) by other effects, for example by solvent effects (Schubert, Shiner). In any event, the delocalization theory of hyperconjugation does not see any uniqueness in H atoms as carriers of hyperconjugation, and the experimental evidence of Taft and others seems to bear out this theoretical expectation.

In their original paper, Baker and Nathan referred to their effect as a "new mechanism of electron release"; electron release was considered an important characteristic and criterion of the effect. However, electron release is not an essential or important feature of the delocalization theory of ordinary (sacrificial) hyperconjugation or conjugation; in this respect it is entirely different from dative hyperconjugation or conjugation, where electron release *is* an essential intrinsic characteristic and criterion. The occurrence of a moderate amount of electron release from a CH_3 group to an unsaturated group in ordinary hyperconjugation is attributable to a somewhat greater electronegativity of the latter than the former. For example in propylene it would correspond to a mild predominance of the resonance structures $H_3^+{=}C{=}CH{-}\bar{C}H_2$ and $H_3^+{=}C^-{-}CH^+{-}\bar{C}H_2$ over $H_3^-{=}C{=}CH{-}C^+H_2$ and $H_3^-{=}C^+{-}C^-H{-}C^+H_2$, all these being accompanied by $H_3^{\cdot}{=}C{=}CH{-}\dot{C}H_2$ and the predominant structure $H_3{=}C{-}CH{=}CH_2$.[1] On substituting a CMe_3 or a CF_3 group for the CH_3 group, the delocalization theory predicts analogous resonance structures, but in the case of the CF_3 group, electron release would be expected to be predominantly *to* it instead of from it because the quasi-π orbitals of F_3 would be more electronegative than the π orbitals of the double bond, opposite to what seems to be true of the quasi-π orbitals of H_3 in the CH_3 group.

In my opinion, doubts and questions about the cause or causes of the Baker–Nathan effect have no conclusive bearing on the general phenomenon of sacrificial hyperconjugation. On the whole, the Baker–Nathan effect, in harmony with other evidence, does seem to support the idea that C—H hyperconjugation is a stronger effect than

C—C hyperconjugation. However, it appears also that the evidence is not very conclusive because of the possibility of other small masking and/or simulating effects.

A further point is that the properties of activated states of hyperconjugated systems, —on which according to rate theory the Baker–Nathan effect usually or often depends, —may not necessarily always parallel those of the ground state, although there is evidence that they usually do. A similar but stronger statement is applicable to conjugated systems.

For electronically excited states of hyperconjugated and conjugated molecules, new considerations enter and can often become important. The properties of electronically excited or ionized states may be expected to differ from state to state and from one type of conjugated or hyperconjugated molecule to another.

(6) The interesting studies of Schubert and collaborators on electronic spectra as presented in this Symposium[5] and in an earlier paper afford a basis for valuable new insight into the theoretical understanding of dative conjugation and hyperconjugation. In agreement with others[6] they interpret the "principal" band spectra of molecules of the type R——X, where R is an alkyl group and X is either a π donor group or the π acceptor group NO_2, as belonging to the category of what have been called intramolecular charge-transfer spectra. It seems fairly sure that this interpretation of the "principal" spectra is reasonably correct, although a thorough theoretical study will be desirable.

The theory of *intermolecular* charge-transfer or donor-acceptor complexes and their charge-transfer spectra, is directly applicable also to molecules stabilized by dative conjugation or hyperconjugation. In an intermolecular charge transfer complex between a π-electron donor and a π-electron acceptor molecule, the association of the two molecules in their ground states to form a complex is explained by the resonance energy associated with resonance between the predominant no-bond structure and a smaller amount of dative structure. From this there follows also the necessity for a complementary excited "charge-transfer" state in which the dative structure is predominant while the no-bond structure is present to a minor extent. A spectroscopic transition from the ground state to the charge-transfer state corresponds to the charge-transfer band. The delocalization theory of dative conjugation, and of the associated charge-transfer spectra, is identical with that of intermolecular charge-transfer stabilization and spectra of π-π complexes, except that here the donor acceptor action involves two π-electron *groups* already bound together by a σ-bond, instead of two separate π-electron molecules.

In the application of this theory to the molecules R— —D studied by Schubert and associates, where D is a π-donor group, the following sets of resonance structures I–IV are those of most importance or interest, for both the ground state and the charge-transfer state. (The number of resonance structures in each set is given in parenthesis after the formula for a typical member of the set.) The structures are written for the case that R is CH_3, but if R is another alkyl group, it is to be understood

[5] W. M. Schubert, R. B. Murphy and J. Robins, This Symposium, p. 199.
[6] S. Nagakura and J. Tanaka, *J. Chem. Phys.* **22**, 236 (1953); *Ibid.* **23**, 1441 (1955); *Ibid.* **24**, 1274 (1956); S. Nagakura, *Mol. Phys.* **3**, 105 152 (1960) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.* A **68**. 601, 969 (1955).

VOL. 17 1962

that C is to be substituted for one or more of the H atoms. Further, for vividness of illustration, D has been taken as an OR group. Besides I–IV, there are also other structures which may be of appreciable importance, especially in the charge-transfer state. There may be considerable admixtures of other excited-benzene-like structures, but probably not enough to alter the conclusions discussed here, but the essential points of interest here can be made by considering structures I–IV only.

I

II

III

IV

In IV, the o indicates an unpaired electron, or also (to a lesser extent) structures with H_3^+ or H_3^- and in each case an opposite charge on the ring. The interaction of structures II and I is dative isovalent conjugation, that of III with I is dative isovalent hyperconjugation, while that of IV with I is ordinary sacrificial hyperconjugation as in toluene. In dative conjugation or hyperconjugation, *one-directional* charge transfer is intrinsic. In ordinary sacrificial hyperconjugation or conjugation, charge transfer occurs more or less equally (if at all appreciably) in both directions.

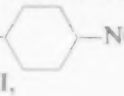
The relative weightings of I–IV in the ground state (N) and in the charge-transfer state (CT) can be estimated *qualitatively* beyond reasonable doubt. For vividness, the following are given as plausible quantitative guesstimates of the fractional amounts of the various structures, with of course no claim to accuracy. Structures I must surely

	I	II	III	IV
N	0·87	0·10	0·02	0·01
CT	0·12	0·72	0·12	0·04

predominate in the ground state, and structures II in the CT state, in agreement with relation (1) as stated in the paper by Schubert and associates. But because the hyperconjugated structure III (an example of Siebold's "anionic hyperconjugation")[5] is hyper-isovalent with II, it can be expected to make a considerable contribution in the CT state, and *certainly* a much larger contribution than in state N. The CT state should therefore be considerably stabilized by structures of type III (and IV) relative to the case where no *p*-alkyl group is present, in which case structure III cannot occur. The ground state, however, should be much less stabilized by these structures.

The frequency ν_{max} of the absorption band corresponding to the transition from N to CT (Schubert's "principal" band) is therefore expected to be decreased when R is substituted for H, exactly as is found by Schubert and collaborators. Thus the delocalization theory of isovalent hyperconjugation furnishes an entirely reasonable and satisfactory explanation of what is observed. Schubert's further observation that the nature of the alkyl group R makes relatively little difference in the observed shift indicates that dative isovalent hyperconjugation of the kind here involved is, at least

for CT excited states, about equally effective whether it be C—H or C—C hyperconjugation. (The observed detailed differences between R groups will not be discussed here.) It does not necessarily follow that the same near-equality must be expected in general. Also, the near-equality here should not be taken as contradicting evidence that C—H hyperconjugation is stronger than C—C hyperconjugation in ground states or in reaction rates.

A similar discussion can be given for Schubert's earlier work on the charge-transfer spectra of molecules of the type R—  —NO_2. Here again we may consider four sets of structures, of types V–VIII,

V

VI

VII

VIII

The interaction of structures VI with V is dative *sacrificial* conjugation, hence should be weaker than that of II with I, where the resonance is isovalent. The interaction of VII with V is dative sacrificial hyperconjugation, that of VIII with V is ordinary sacrificial hyperconjugation as in toluene. The following are guesstimates of the weightings of V–VIII in the N and CT states of the *p*-alkyl nitrobenzenes. In these molecules, structures VIII and VII are *both* hyperisovalent with VI (*all* are sacrificial relative to V), so that the ordinary hyperconjugation structures VIII should be more prominent here than the corresponding structures IV, which are sacrificial relative to I–III for molecules R— —D.

	V	VI	VII	VIII
N	0·95	0·03	0·01	0·01
CT	0·03	0·60	0·15	0·24

Just as in molecules of type R— —D, extra structures (here VII and VIII) are introduced by the presence of the *p*-alkyl group, and these must unquestionably be much more important for the CT than for the N state, so that the former should be stabilized more than the latter, and ν_{max} for the CT ← N absorption process should again be decreased, just as has been observed by Schubert and collaborators.

It is seen that the π-electron delocalization theory of hyperconjugation, as approximated here in terms of resonance structures, gives a straightforward and unambiguous explanation of the lowering of the frequency of the charge-transfer band by *p*-alkyl substituents in both donor-group-substituted and acceptor-substituted benzenes.

As has already been stressed in Comment (5), the π-electron delocalization theory

of ordinary sacrificial hyperconjugation does not require the methyl or other alkyl group (as e.g. in toluene or t-butylbenzene) to be intrinsically either a quasi-π electron donor or a quasi-π acceptor. *Both* structures should be present in nearly equal but perhaps relatively small amounts (the predominant hyperconjugative structure in that event being the long-bond structure); but the weight of evidence seems to indicate that in ordinary sacrificial hyperconjugation the donor function of the alkyl group (or at least of the methyl group) does predominate somewhat. (At the same time, these groups release electronic charge fairly strongly by the *inductive*, i.e. σ-bond, route.)

Structures III and VII (hyperisovalent respectively with II and VI) show alkyl groups functioning respectively as electron acceptors and as electron donors in *dative*-hyperconjugative resonance structures which must be of appreciable importance in stabilizing charge-transfer states. This amphoteric functioning of the alkyl group, with its charge transfer direction governed by whether the other substituent is a strong electron donor or acceptor, is entirely reasonable and consistent with the theory of sacrificial hyperconjugation according to which in the *absence* of strong direction neither the donor nor the acceptor role is strongly emphasized.

C. A. Coulson

Comments on paper by D. R. Lide

DR. LIDE throws almost all the responsibility for bond length changes in carbon bonds on to changes of hybridization. I believe this to be one of the important factors, but the effect must be more subtle than is sometimes supposed. Thus, changes of hybridization in an isolated carbon atom make no difference whatever to the first-order density matrix. If we make any four orthogonal hybrids out of $sp_xp_yp_z$ the resultant charge-cloud is still spherically symmetrical. Thus hybridization can only achieve its effect in terms of the second-order density matrix, and presumably even here it is largely a question of the difference between the electron correlation terms for electrons with coupled, or with random, spins. When the matter is thought of in terms of the electron density, it is surprising that such characteristic differences are found as is shown by experiment. My own opinion, therefore, is that either we should be content with a very simple type of presumed relation between hybridization and bond length, or we must look for a much more sophisticated analysis, in which even the concept of hybridization may not be adequate.

A situation of the kind just described would not apply to atoms where there is a lone-pair of electrons (e.g. NH_3). For here we have what Moffitt called second-order hybridization, and even the single particle density function is dependent on the hybridization parameters.

C. A. Coulson

Comments on paper by B. P. Stoicheff

ONE of the most disturbing features of this very interesting paper is the observation that although in many cases the electron-diffraction and spectroscopic values agree excellently, yet for CH and CD in CH_4 (and CD_4), they differ by an amount between 0·010 and 0·020 Å. What can be the origin of this difference, which is of the order of magnitude of one-half the classical amplitude of vibration! Further, why is the diffraction value larger than the spectroscopic one, when the following argument would

lead us to expect the opposite? The spectroscopic bond length is based on moments of inertia, and therefore is determined almost entirely by the nuclei. We may say that this gives a very reliable length (suitably averaged, of course!) for the internuclear distance. The electron diffraction value involves both nucleus and charge-cloud. So far as the nucleus is concerned, the agreement with spectroscopic measurements should ideally be almost perfect. But so far as the charge-cloud is concerned, we should expect small differences depending on the lack of spherical symmetry in the electron density around an atom. In the case of the H and D atoms, conventional valence theory leads us to suppose that any charge migrations that may take place as a result of the formation of a molecule, will be such as to attract charge into the region between the nuclei. This would be expected to give the appearance of a shorter bond rather than a longer one. Dr. Stoicheff has been very careful not to offer any "explanation" of the effects which he has catalogued and analysed. Does he have any comments to make on the unexpected situation for CH bonds in methane just described?

VOL. 17 1962

B. P. Stoicheff

Reply to comments by C. A. Coulson

THE discrepancy to which Dr. Coulson refers is probably correctly interpreted by Bartell, Kuchitsu and De Neui (reference 31) as arising from the different averages over the zero-point vibrations inherent in the two methods. The above authors have computed corrections to the diffraction "r_g" and spectroscopic "r_0" values (by *assuming* a modified anharmonic Urey–Bradley force field) which result in similar *calculated* values of the equilibrium bond length in methane.

The effect which Dr. Coulson mentions while undoubtedly present would perhaps be expected to produce only a small difference in apparent bond lengths. Unfortunately the experimental data and our knowledge of potential functions of polyatomic molecules are too limited to look for such interesting effects. As a first step in understanding the difference between diffraction and spectroscopic values of bond lengths I believe it would be very useful to obtain electron diffraction data on diatomic molecules for comparison with existing spectroscopic data.

D. R. Lide

Comments on the paper by B. P. Stoicheff

DR. STOICHEFF has raised a question about the C—C distance in isobutane. He states that the value of 1·525 Å [*J. Chem. Phys.* 33, 1519 (1960)] might be in error by as much as 0·007 Å because of the small z co-ordinate of the off-axis carbon atoms. In fact, there is no reason to suspect an error of this magnitude. Since almost three-quarters of the total mass of the molecule is in the plane of the off-axis carbons, this plane must necessarily lie close to the center of mass. This type of molecule is clearly distinguished from a case such as propylene, where the central carbon atom lies near a principal axis for rather accidental reasons (i.e. because of an approximate balancing of the other masses in the molecule). As an independent check one may calculate the z co-ordinate of the off-axis carbons from the first-moment relation; the change in the C—C distance is completely trivial (specifically 0·0004 Å).

There is strong evidence, then, that the r_s value of the C—C distance in both isobutane and propane is very near 1·526 Å. The distance in ethane is much less certain.

The values of 1·534 Å and 1·539 Å obtained from infrared and rotational Raman spectra, respectively, do not agree as well as they should. Furthermore, these are mixed r_s and r_0 values, and it has been pointed out that the true r_s distance might be as much as 0·008 Å lower. Thus there is no clear evidence at this time for a discrepancy between the ethane and propane–isobutane values. Ethyl fluoride should be excluded completely from these comparisons. Here the location of the central carbon atom could not be experimentally determined, and it was arbitrarily assigned a co-ordinate of zero. The resulting C—C distance could be in error by as much as 0·02 Å.

B. P. Stoicheff

Reply to comments by D. R. Lide

I AM grateful to Dr. Lide for pointing out the difficulty in the determination of the C—C bond length in ethyl fluoride:[52] a calculation shows the uncertainty in this value to be about 0·010 to 0·020 Å and therefore this bond length should be deleted from Table 3.

The source of this difficulty in the ethyl fluoride structure[52] illustrates my point that the C—C bond length in isobutane may be slightly longer than the quoted value of 1·525 Å. In ethyl fluoride it is found that the moment of inertia *decreases* by 0·0064 a.m.u. Å^2 when ^{13}C is substituted for ^{12}C in the near-axis position. This anomaly is of course a consequence of zero-point vibrations. There is no reason to expect a smaller effect when substitution is made on a C atom no matter what its position in a molecule. Thus if we assume a similar decrease in the moment of inertia in propylene[57] the r_s coordinate for the central C atom becomes 0·112 Å rather than 0·081 Å and is in good agreement with the preferred value of 0·106 Å obtained from the first moment equation.[57] A similar zero-point vibration effect in isobutane leads to a C coordinate of 0·126 Å instead of 0·102 Å and results in a C—C bond length of 1·532 Å. Unfortunately, the evidence from the first moment equation is not completely convincing here because of the assumptions regarding the internal as well as the axial symmetry of three CH_3 groups. In conclusion it may be said that the C—C bond lengths in ethane and isobutane are somewhat uncertain but the uncertainties are such as to bring both closer together.

C. A. Coulson

Comments on paper by O. Bastiansen and M. Traetteberg

(1) I SHOULD like to ask Professor Bastiansen whether he can give any reason why the "single" bond in cycloöctatetraene should be 0·021 Å shorter than in butadiene. It is hard to avoid the conclusion that some sort of resonance is operative in the ring molecule, not equally operative in the chain.

(2) Professor Bastiansen has raised the important question of the possible existence of attractive (as well as repulsive) forces between non-bonded atoms such as the halogens in 2,2′-dihalobiphenyls. It may be worth mentioning that in force-constants analysis of the vibrations of several molecules, notably the group V trihydrides, indications of such attractive forces have sometimes been found. If this is indeed the case with the *ortho*-biphenyls then the total potential energy curve as a function of the

angle θ of twist of the two halves, measured from zero in the *cis*-form may sometimes be as shown in the diagram. Here:

curve 1 is the resonance energy curve
curve 2 is the steric repulsion curve
curve 3 is the dispersion (?) attractive force,
with its minimum in the *cis*-position.

The final curve 4 shows minima at some fairly small value of θ, and also at $\theta = \pm \pi$. But they are not of equal height.

O. Bastiansen

Reply to comments by C. A. Coulson

I AM afraid I cannot give a good explanation for the mentioned difference in bond distance. I agree with Professor Coulson that it is difficult to avoid the conclusion that some sort of resonance characteristic for the ring molecule must take place. As stated in our article the effect may perhaps be related to the cyclic form of cycloöctatetraene that might favor *p*-electron delocalization. This "cyclic" resonance effect must be so large as to over-compensate for the loss in resonance due to the less effective *p*-electron overlap in cycloöctatetraene compared to that in butadiene.

W. M. Schubert

Comments on paper by O. Bastiansen and M. Traetteberg

(1) THE finding that the 2,2′-halobiphenyls prefer a near *cis* instead of a near *trans* conformation is a convincing case for the operation of a dispersion force (i.e. van der Waals attractive force). However, it is not clear whether the main attractive force is between an *ortho*-halogen and the π-system of the attached ring (attraction presumably at a maximum for a 90° interplanar angle) or between *ortho*-halogens, although probably the latter. If the latter, the increase in interplanar angle in the order F < Cl < Br < I would speak for an important underlying van der Waals repulsion.

(2) Does the statement to the effect that the planar *trans*-form of 2,2′-bipyridyl should be free of steric strain (also appearing in the paper by Cruickshank) take into account the unshared electron pair on each nitrogen? i.e. what is the van der Waals repulsion radius of the N: as compared to aromatic C—H?

O. Bastiansen

Reply to comments by W. M. Schubert

IN the case of the 2,2′-dihalobiphenyls, we believe the halogen–halogen interaction to be responsible for the near *cis* conformation. It is no doubt correct to include the interaction between the halogen atoms and the π-system of the attached ring; though this interaction is probably less important than the halogen–halogen interaction as also stated by Schubert.

Schubert's question on the 2,2′-bipyridyl is indeed a justified one. In our paper, we were considering the kind of steric hindrance that occurs in the biphenyl derivatives where a planar molecule has to suffer a severe steric strain. What we wanted to express was the fact that the interaction between the two *ortho*-hydrogen atoms is effective only in the *cis* region. In the other possible conformations of the molecule, other

effects, such as resonance, should be expected to be predominant. Comparing the two effects to be expected in the *trans* region, namely resonance and hydrogen–nitrogen interaction, our electron diffraction data seem to demonstrate that the resonance energy is not large enough to keep the molecule in the planar form. A possible hydrogen–nitrogen repulsion seems in other words to be of greater importance in the *trans* region conformations than resonance. The hydrogen–nitrogen distance in the planar *trans* form is, in fact, a little shorter than the corresponding Pauling–van der Waals distance. Without a closer study of the effect, it is difficult to decide in which angle region the van der Waals hydrogen–nitrogen is attractive and in which, if any, it is repulsive. A simple consideration seems indeed to indicate a minor repulsion in the planar *trans* conformation as implicitly suggested in Schubert's question.

I am indeed grateful to Dr. Schubert for having raised this question. The point we wanted to stress, namely the inability of resonance to secure a planar molecule, may have been lost as the effect of our misleading statement. It would no doubt be an interesting undertaking to try to calculate the potential energy as a function of the angle of twist including hydrogen–hydrogen interaction, hydrogen–nitrogen interaction, and resonance.

C. A. Coulson

Comments on paper by D. W. J. Cruickshank

CRUICKSHANK has shown that the simplest of all MO theories gives pretty good results for most bond lengths. But there are residual discrepancies with experiment. It may be mentioned that Dr. A. Golebiewsky and the writer, in some work in course of publication, have shown, using quite simple ideas of self-consistence, that by allowing for the variation of the resonance integral β with bond length, and by including the effect of the underlying σ-bond, the discrepancies can be considerably reduced. In the case of butadiene, which must be regarded as one of the most severe tests of any theory, since the disparity between the short and long bonds is greater than in ring molecules, the theory of Golebiewsky and Coulson reduces the average error from about 0·03 Å to about 0·01 Å. This value seems to be about the best that can be achieved, with theory or experiment, at the moment.

C. A. Coulson

Comments on paper by D. J. Marais, N. Sheppard and B. P. Stoicheff

EVEN if it is agreed that the bond length for the central "single" bond in butadiene is not much shorter than a conventional sp^2—sp^2 trigonal σ-bond, we are still left with the problem of understanding the planarity of butadiene. If butadiene is written as two non-interacting double bonds ^{1}—^{2} ^{3}—^{4}, then the π-electrons on atoms 2 and 3 would be pairs to other π-electrons (on 1 and 4 respectively) and there would then be the usual repulsion between non-paired electrons which would tend to destroy planarity. Indeed several years ago now, J. Guy [*C. R. Acad. Sci., Paris* **223,** 85 (1946)] showed that this structure, which is merely the conventional Kekule structure for butadiene, would not be planar, since the repulsion of these π-electrons would tend to rotate the two halves relative to each other around the 2—3 bond. This effect is well known for H_2O_2 and N_2H_4, where of course there are two lone-pair electrons on each atom. Even if the argument is not now so strong as it seemed in 1946, it is still true

that without some form of conjugation across the central bond it remains rather difficult to understand the high planar stability of butadiene. In present-day views, what is the origin of this stability, if it is not some measure of conjugation?

Is it unreasonable to accept something like the value 1·515 Å. for the pure sp^2—sp^2 σ-bond, as in Bastiansen's paper, applicable to hexaphenylbenzene? If so, there is a shortening of 1·515–1·476=0·04 Å. in this central bond.

C. A. Coulson

Comments on paper by L. Oleari

It is at first sight surprising that the single-configuration single-center wave function of Oleari gives so good an energy: and yet the much more complex wave function of Saturno and Parr [*J. Chem. Phys.* **33,** 22 (1960)] on which the paper by Turner *et al.* is based, does not improve it as much as one would have hoped. I believe that the trouble lies essentially in the situation around the four H atoms. For there is a singularity in the Hamiltonian at these points, and so, in the language used by Roothaan and Weiss [*Rev. Mod. Phys.* **32,** 194 (1960)] and Kolos and Roothaan [*Rev. Mod. Phys.* **32,** 205 (1960)], there will be certain cusp conditions to be satisfied by the correct wavefunction. It may be shown, in general terms, that at each nucleus where any one electron experiences a nuclear charge Ze, the wave function for any one electron must satisfy the condition

$$\langle \partial\psi/\partial r \rangle = -Z\psi,$$

where the left-hand side denotes the mean value of the outward gradient of ψ over the surface of a small sphere surrounding the nucleus. If there is spherical symmetry, then of course $\partial\psi/\partial r$ is independent of angular direction, and we reach the condition easily verified for hydrogenic orbitals:

$$\frac{\partial\psi}{\partial r} = -Z\psi$$

It is exceedingly difficult to represent a function which has a discontinuity of slope at some given point in terms of functions based on some other point as origin. Thus it is to be expected that a large number of terms will be needed to deal with this singularity alone, quite independently of any electron-correlation effects which we know will be important. Precisely this situation has been carefully investigated by M. Cohen and the writer [*Proc. Camb. Phil. Soc.* **57,** 96 (1961)], where, in the case of H_2^+, using a single-centre model, the effect of introducing more and more terms in a trial wave function showed itself almost entirely in a closer approximation near the nuclei. It seems reasonable to hope, therefore, that if the conventional single-centre type of expansion for methane could be supplemented by a single term that would allow for the discontinuity in grad ψ, and more nearly satisfy the cusp condition, considerable improvement in the wave function might be obtained fairly easily. Such a term could be

$$A\{e^{-cr_a} + e^{-cr_b} + e^{-cr_c} + e^{-cr_d}\}$$

where $r_a \ldots r_d$ denotes distances from the four protons. The cusp condition would be that

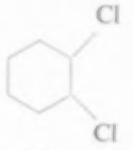
$$\{cA = \psi(0)\}$$

where $\psi(0)$ is the value of ψ at a proton.

C. A. Coulson

Comments on paper by L. S. Bartell

QUITE irrespective of whether or not we agree with the particular application of his ideas to the difference between carbon–carbon bonds of varying hybridization, there is no doubt that Bartell is right in drawing attention to the importance of non-bonded interactions. These may be either attractive or repulsive, with repulsive forces usually predominating. The origin of these forces, in any but the simplest pseudo-atomic systems, is exceedingly complex. Thus in the *ortho*-dichloro-benzene molecule, there will be chlorine-chlorine forces of the following kinds:



(i) electrostatic repulsion between effective net charges on the two chlorines,

(ii) attraction due to resonance with structures showing Cl—Cl as a single bond,
(iii) overlap repulsion between the charge-clouds of each separate chlorine atom,
(iv) dispersion forces of attraction between the chlorines,
(v) "random-spin" repulsions of the electrons not paired to each other in the two chlorines,
(vi) interactions due to dipoles and higher multipoles in the C—Cl bonds, and smaller contributions from more remote parts of the molecule.

Some of these forces have been investigated by Stocker and myself (C. A. Coulson and D. Stocker, *Mol. Phys.* **2**, 397 (1959); C. A. Coulson, Chemical Society, Kekule Symposium, London, 1958; Butterworths Scientific Publication).

But the series of contributions (i)–(vi) counts certain types of interaction more than once, and any complete unequivocal separation of the total interaction into contributions of this kind seems at present quite impracticable. It is my impression that the study of these forces between non-bonded atoms may well play a dominant role in molecular-structure calculations of the next ten years.

W. M. Schubert

Comments on paper by L. S. Bartell

THE intriguing non-bonded interactions hypothesis of Bartell is at least qualitatively consistent with the decrease in C—C bond length with a decrease in the number of substituents on the two carbon atoms. However, the hybridization hypothesis of Dewar and Schmeising seems to more simply accommodate the observation that C—C bond lengths cluster about discrete values according to whether the carbons can be labeled as tetrahedral, trigonal or digonal. Bartell's argument that there is a close balance of the postulated considerable repulsive forces between substituents attached to the same tetrahedral (or trigonal) carbon atom is used to account for C—C shortenings depending apparently only on the *number* of repulsions, and also answers other questions that could be raised. Although Bartell's calculations based on intermolecular van der Waals force laws may indicate there is a balance of repulsive forces, it is nevertheless difficult to imagine why this should be so. i.e. what are the underlying "theoretical" reasons why, e.g. in the variation of say one of the substituents on a tetrahedral or trigonal carbon, the bond length of the varying substituent (of discrete

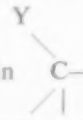
length for any tetrahedral, trigonal or digonal carbon-substituent), the bond angles, and possibly the bond lengths to the remaining fixed substituents (but not for carbon-substituents), should so adjust as to maintain such a balance?

The interesting relief of strain explanation offered for the β-deuterium kinetic isotope effects found by Lewis and by Shiner in solvolysis reactions appears offhand to contradict the balance of repulsion forces argument. That is, the isotope effect is attributed to an *imbalance* of repulsive forces between isotopic species in the tetrahedral ground state and in the transition state, which is on the way to becoming tetrahedral. It is true that only a small imbalance of repulsive forces need be required to account for the small $\Delta H^{\ddagger}$ differences between the isotopic compounds. But if the imbalance created by a considerable substituent change (e.g. hydrogen to chlorine) is supposed to be small, then a change in substituent from hydrogen to deuterium must create an extremely small imbalance of repulsive forces.

VOL. 17 1962

L. S. Bartell

Reply to comments by W. Schubert

THE points raised by Dr. Schubert emphasize the need for consideration of the magnitudes of effects involved. His reservations center chiefly upon the forces between X and Y groups in  C—X. In reply, it may be said that no such rigid balance is required of the non-bonded model as Schubert implies. The C—X bond length and energy may very well vary somewhat with the nature of Y as well as with the number of repulsions. Brief conjectures about this were made in my paper but the documentation of such variations is very meager. Even the principal variations treated in the paper are not much larger than common experimental errors.

A rationalization of the approximate balance (i.e. the relative insensitivity of X. . .Y interactions to the nature of Y) is given in my comments on Professor Wilson's paper. No detailed readjustments of bond lengths and angles of the sort envisioned by Dr. Schubert are required. Several observations suggest that the balance is not exact. If isomerization energies of paraffin hydrocarbons are non-bonded in nature, our model requires $(V_{CC} + V_{HH} - 2V_{CH})$ to be about 1·3 kcal/mole. Bond angles imply similar imbalances.

As a rule X. . .Y forces seem to be of the order of 0·1 md, X. . .Y potential energies of the order of 3 kcal/mole, and C—Y force constants, perhaps a few md/Å. Imbalances of several hundredths md should not seriously invalidate the essence of the simple model. The imbalance involved in the β-deuterium isotope effect, which appeared to Schubert to contradict our hypothesis, is actually only about 0·001 md, and consequently, of no concern in the broad picture. This small distinction between CH_3. . .Y and CD_3. . .Y forces, which is predicted by the non-bonded model, is nevertheless sufficient to account roughly for the observed isotope effect. The difference between the presence of a CH_3 group and its complete absence, as essentially occurs in the comparison of $(CH_3)_2CH$—C and CH_2CH—C, represents a change in C. . .C interactions one hundredfold greater. It was this type of change with which the present work was primarily concerned.

In conclusion, it is fair to remark that the main value of the simple non-bonded model is more in the forceful attention it draws to the possible magnitude of the universally neglected interactions than in its reliable handling of them. It is not difficult to find arguments to the effect that the model may be spurious and that the bond and unshared electron distributions rather than atom-atom interactions must be vitally important. Consider the fact (see reference 28) that the plucking of hydrogen atoms from H_2O, NH_3 or CH_4 lengthens rather than shortens the remaining bonds, even though the number of non-bonded repulsions is reduced. In partial defense of the nonbonded model, it may be mentioned that the resolution of experimental F matrices into components (reference 18) renders this lengthening compatible with the existence of nonbonded repulsions. The stretch–stretch bond interactions imply the correct magnitude of bond lengthening when adjacent bonds are severely stretched. Conversely, they also correctly imply the more easily understood shortenings of bonds when adjacent bonds are shortened, the limit being reached at the united atom stage, HF. Clearly, the non-bonded model must be used with caution.

L. S. Bartell

Comments on the paper by E. Bright Wilson, Jr.

PROFESSOR WILSON's opinion that the roles of steric influences, conjugation, and hybridization cannot be very definitively assessed at present seems to be shared by many of the contributors to this symposium, including myself. His conclusion in the abstract that "the steric theory is probably untenable", however, appears to me at least as speculative as the steric theory itself, in view of the meager evidence he has cited against it.

The principal virtue of the "steric theory" (or, as I regard it, the hypothesis that *intramolecular* nonbonded interactions follow roughly the same force laws as are ascribed to their *intermolecular* counter parts) is that it correlates, semi-quantitatively, a wide variety of known effects in an extremely simple way. It is as yet far from rigorous, and it must be emphasized that not one correlation it makes is in itself an unequivocal demonstration of the validity of the hypothesis. Therefore, it is of interest to examine Professor Wilson's arguments against the model. They are, as I see them:

(a) Our ignorance of nonbonded potentials is very great.

(b) It would be remarkable if different substituents did not lead to markedly different results.

(c) Barriers to rotation are not steric.

(d) The naive "hard sphere" model of bond angles works no better than the naive hybridization model.

Point (a), of course, cannot rule out the steric model. The balance of repulsions involved in point (b), briefly mentioned in my paper, can be rationalized in terms of Pauling's observation that van der Waals radii are not chaotically scattered but rather are closely related to covalent radii. Pauling's relation, coupled with the usual empirical approximations for nonbonded interactions, suggests a considerable compensation for variations in atomic size of substituents. Larger atoms are associated with correspondingly larger nonbonded distances in the carbon environments of most concern to us. It is fair to admit, however, that the literature dealing with steric interactions is inadequate to settle the exact amount of compensation. Point (c) of Professor Wilson

is almost surely true, as he has shown so beautifully in his recent research, but this implies no incompatibility with the steric model. The repulsions I invoke are an order of magnitude *too small*, at least in ethane, to account for the barrier. Finally, the excessive oversimplifications of the models in point (d) render any very subtle comparisons inconclusive. The "hard sphere" model was introduced originally simply to point out that it provides an alternative description to the well-known constant-angle model discussed by Wilson, and one strongly smattering of "steric" influence. Having served as a brief introduction to the idea of intramolecular interactions, it was discarded in the original paper in favor of a model with a more reasonable force law.

VOL. 17 1962

Nevertheless, it is interesting to note that the simplest steric model works remarkably well even for the recent data cited by Professor Wilson, except for angles involving hydrogen. If hydrogens are excluded, the angles show a mean deviation of only about 1°, a scatter no greater than the errors in the data from which the sphere radii were assigned. The spectroscopists clearly have difficulty with hydrogen positions (they are not alone in this respect!) and errors of several degrees are not unknown. Accordingly, the poorness of fit with hydrogen may not be solely the fault of the model. On the other hand, the model does not appear sufficiently fundamental to be worth more detailed consideration at present.

Additional evidence that steric effects influence bond angles has been presented by A. I. Kitaigorodskii. (*Abstract G. S.* III 2, Federov Session on Crystallography, Leningrad, U.S.S.R. May 25, 1959) Kitaigorodskii successfully correlated variations in bond angles in a large number of organic molecules using nonbonded potential functions similar to those I invoke. Also, contrary to the first impression of many chemists with regard to the probable direction of steric effects, the fact that the C—C—C angle in isobutane is larger than 109·5° but *smaller* than that in propane [D. E. Lide, *J. Chem. Phys.* **33,** 1514, 1519 (1960)] is accounted for by a steric model, and the presently considered potential functions [L. S. Bartell, *J. Chem. Phys.* **32,** 827 (1960)] yield fair quantitative predictions of the angles.

The present nonbonded model is subject to serious criticism in its oversimplified representation of molecular force fields. Nonetheless, the evidence against it seems as yet insufficient to warrant rejecting the basic idea.

W. M. Schubert

Comments on paper by E. B. Wilson, Jr.

WITH regard to two of Wilson's arguments against the hybridization hypothesis: firstly, a possible role of conjugation in C—X bonds does not necessarily extrapolate to C—C bonds in which no "unshared" electron pairs are involved, as nicely pointed out in the paper by Lide; secondly, the Dewar hypothesis does not require that C—H bond distances vary with hybridization to the same extent as C—C distances. In fact, a smaller variation in C—H bond distances would perhaps be more consistent with the smaller variation in C—H than C—C bond energies that are required in the Dewar hypothesis to account for the stabilization energy of butadiene, etc. In that connection, a smaller variation in the C—H bond energy with hybridization could be due in part to the electronegativity of hydrogen being greater than that of tetrahedral carbon. In that event, that part of the changes in the C—H bond energies from tetrahedral to trigonal to digonal carbon that are due to changes in Pauling-like Δ values would be

smaller than considered by Mulliken [*Tetrahedron* **6**, 68 (1959)] who used electronegativity order: tetrahedral carbon > hydrogen.

G. L. Caldow and C. A. Coulson

Comments on paper by L. Pauling

IN connection with Pauling's discussion of the repulsive effects of lone-pair electrons on the bond energies of molecules, we should like to report some recent calculations[1] which we have made for the halogen diatomic molecules, and which are concerned with similar effects. In these halogens, the sequence of bond energies (see Table 1)

TABLE 1. BOND ENERGIES IN THE HALOGEN MOLECULES (kcal/mole)

	F_2	Cl_2	Br_2	I_2
Experimental dissociation energy D	37·7	57·1	45·4	35·6
Calculated Coulomb energy Q ($+e$ for attraction)	10·3	42·8	37·6	30·2
Empirical exchange energy ($D - Q$)	27·4	14·3	7·8	5·4

is $F_2 < Cl_2 > Br_2 > I_2$, in which the position of fluorine seems anomalous. We have made some crude valence-bond calculations which seem to suggest that this anomalous sequence arises from the Coulomb term rather than from the exchange term.

If the energy of a two-electron homonuclear molecule is written in the conventional way

$$E = 2E_{\text{atom}} + \frac{Q + J}{1 + S^2}$$

it may be transformed to

$$E = 2E_{\text{atom}} + Q + \frac{\eta}{1 + S^2} \tag{1}$$

where η may be called[2] the effective exchange integral, or bond integral, and S is the overlap integral. The bond energy is

$$Q + \eta/(1 + S^2) \tag{2}$$

where Q, the Coulomb energy, is given by

$$Q = \iint \varphi_A(1)\varphi_B(2)\,\{\mathrm{H} - 2E_{\text{atom}}\}\,\varphi_A(1)\varphi_B(2)\,d\tau_1 d\tau_2$$

$$S = \int \varphi_A(1)\,\varphi_B(1)\,d\tau_1$$

With a many-electron homonuclear molecule, simple generalizations of (1) and (2) are necessary. The Coulomb energy Q now takes the form

$$Q = \int \psi_A(1,2,\ldots n)\,\psi_B(n+1,\ldots 2n)\,\{\mathrm{H} - 2E_{\text{atom}}\}\,\psi_A(1,\ldots n)\,\psi_B(n+1,\ldots 2n)\,d\tau^{2n} \tag{3}$$

There are somewhat similar expressions for J, η and S, though J now includes repulsive

[1] G. L. Caldow and C. A. Coulson, in course of publication.
[2] S. Fraga and R. S. Mulliken, *Rev. Mod. Phys.* **32**, 254 (1960).

exchange interactions between non-paired orbitals, as well as attractive ones between the paired ones. In (3) ψ_A and ψ_B are the leading diagonal terms in each separate determinantal atomic wave function. Thus in the evaluation of Q we have the mutual repulsion of the two separate atomic charge-clouds, together with the attraction of each charge-cloud for the other nucleus, modified of course by the mutual repulsion of the two nuclei. If there is substantial penetration of one charge-cloud by the other, then the attraction terms (which result essentially from the fact that electrons are being pulled towards two nuclei rather than one) may outweigh the repulsions. This is precisely what we have found.

Thus, assuming pure p σ-bonds, and using Slater orbitals with no hybridization, we find the Q-values shown in the table. These are all of such a sign as to contribute positively to the binding energy. What seems to us to be interesting here is that this sequence of Q-values is the same sequence as that of the experimental binding energies, and indeed if we suppose that the difference between the two is due entirely to the effective exchange integral term corresponding to $\eta_i/(1 + S^2)$ in (1), then we obtain the smooth set of values shown in the last row of the table. There is now no anomaly in the case of F_2.

It would be nice to be able similarly to calculate the effective exchange terms and verify this variation of η. But not only are these terms more difficult mathematically, they are also more strongly dependent on the assumed form of the orbitals, and the extent of hybridization.

Insofar as our present calculations are significant, they suggest that in many-electron molecules, the generalized Coulomb integral may be dominant in determining the variation of bond energy in a related series of molecules. In the case of the halogens, the low value of $Q(F_2)$ is to be associated with the fact, often pointed out by earlier workers, that the size of the valence-shell orbitals is smaller than would be expected on the basis of an entrapolation from the other members of the series. As a result there is less penetration, and less electrostatic attraction. Our conclusions differ somewhat from those for N_2 in Pauling's paper: for it seems that Pauling pays no attention to Q, and throws all the responsibility for bonding on to the exchange terms. In many cases, of course, Q and J will be expected to vary similarly. Further calculations of both quantities for other molecules will be needed to settle precisely which is normally the more important.

L. S. Bartell

Comment on paper by Inga Fischer-Hjalmars

SOME time ago, in a study of isotope effects, I made calculations on biphenyl similar to those by Miss Fischer-Hjalmars. Since I used the nonbonded interaction potentials [*J. Chem. Phys.* **32**, 827 (1960)] referred to in my present paper rather than Hills' potentials [*J. Chem. Phys.* **16**, 399 (1948)], it may be of some interest to compare results to illustrate the range of error introduced by our ignorance of the precise form of the potentials. Calculations were made assuming undeformed benzene-like rings with an inter-ring conjugation energy represented by $V_0 \cos^2 \theta$, a function quite similar to that adopted by Miss Fischer-Hjalmars. If V_0 was taken to be 4 kcal/mole, the equilibrium twist angle, using only H. . .H interactions, was found to be about 39° (cf. the experimental value of 42 $\pm$ 10°). The enhancement of repulsions by zero-point vibrations was found to increase the angle by an additional 1 or 2 degrees (the enhancement for

the deuterated species was half a degree smaller). When C. . .H forces were included the angle opened up to about 42°. The equilibrium twist angle was relatively insensitive to V_0, varying by only 5° when V_0 varied by 50%. The potential hill of the planar conformation was appreciably higher than that of Miss Fischer-Hjalmars, being several kcal/mole, but this value was sensitive to the stress-relieving distortions of bond angles anticipated to occur at zero twist.

For several reasons I have reservations about potentials involving hydrogens constructed, as were Hill's, associating a hydrogen van der Waals packing diameter of 2·4 Å with the minimum of a Buckingham or 6–12 potential function. This seems to make hydrogens too small and too "hard". For that matter, my own potentials are essentially based on speculation although they correlate many facts. It is to be hoped that much more attention will presently be given to the calculation of potential functions that we can use with greater confidence.

VOL.
17
1962